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(54) Title: COATED ARTICLES

(57) Abstract: The invention relates to novel composite materials comprising (a) an inorganic or organic bulk material having attached to its surface at least one polyionic material that comprises covalently bound initiator moieties for radical polymerization; and (b) a hydrophilic surface coating obtainable by applying one or more different ethylenically unsaturated hydrophilic monomers or macromonomers to the bulk material surface provided with the initiator radicals and polymerizing said monomers or macromonomers. The composite materials of the invention have desirable characteristics regarding adherence to the substrate, durability, hydrophilicity, wettability, biocompatibility and permeability and are thus useful for the manufacture of biomedical articles such as ophthalmic devices.

Coated Articles

The present invention relates to coated articles such as biomedical articles, especially contact lenses, which are at least partly coated with a hydrophilic polymer, and to a process for the manufacture of said coated articles.

A variety of different types of processes for preparing hydrophilic polymeric coatings on an "inert" hydrophobic substrate have been disclosed in the prior art. For example, WO 99/57581 discloses to first of all provide the article surface with covalently bound photoinitiator molecules, coating the modified surface with a layer of a polymerizable macromonomer and then subjecting it to a heat or radiation treatment whereby the macromonomer is graft polymerized thus forming the novel article surface. The covalent binding of the photoinitiator molecules to the article surface is created by first subjecting the article surface to a plasma treatment thereby providing the surface with functional groups, and then reacting said functional groups with coreactive groups of a functional photoinitiator.

A plasma treatment requires a considerable investment in equipment and is furthermore difficult to be integrated in an automated production process. For example, a plasma treatment requires that the article to be treated is dry before exposure to the plasma. Thus, a polymeric article such as a contact lens that is wet from prior hydration or extraction must be dried previously, thereby adding time in the overall lens production process as well as imposing added costs of obtaining a drying equipment.

Therefore, it would be highly desirable to modify the surface functionalization step of the process disclosed in WO 99/57581 such that the plasma treatment is avoided and replaced by a technique which is easy to perform with standard equipment and which is thus more feasible for an automated production process.

Surprisingly, it has now been found, that hydrophobic articles may be readily functionalized by adding at least one polyelectrolyte or preferably a bilayer of functional polyelectrolytes to the article surface. The functional groups of the polyelectrolytes that are adsorbed and/or heteropolarly bound on the surface then may be used for the covalent attachment of

polymerization initiators which in turn may initiate the graft polymerization of suitable hydrophilic monomers or macromonomers onto the article surface.

The present invention therefore in one aspect relates to a composite material comprising (a) an inorganic or organic bulk material having attached to its surface a polyionic material that comprises covalently bound initiator moieties for radical polymerization; and (b) a hydrophilic surface coating obtainable by applying one or more different ethylenically unsaturated hydrophilic monomers or macromonomers to the bulk material surface provided with the initiator radicals and polymerizing said monomers or macromonomers.

The bulk material underlying the composite materials of the invention is preferably a material that is devoid of ionic groups such as cationic or anionic groups. Accordingly, the surface of the preferred bulk materials is also devoid of ionic groups such as carboxy, sulfo, amino and the like groups and is thus substantially free from ionic charges.

Examples of suitable bulk materials are quartz, ceramics, glasses, silicate minerals, silica gels, metals, metal oxides, carbon materials such as graphite or glassy carbon, natural or synthetic organic polymers, or laminates, composites or blends of said materials, in particular natural or synthetic organic polymers or modified biopolymers which are known in large number. Some examples of polymers are polyaddition and polycondensation polymers (polyurethanes, epoxy resins, polyethers, polyesters, polyamides and polyimides); vinyl polymers (polyacrylates, polymethacrylates, polyacrylamides, polymethacrylamides, polystyrene, polyethylene and halogenated derivatives thereof, polyvinyl acetate and polyacrylonitrile); or elastomers (silicones, polybutadiene and polyisoprene).

A preferred group of materials to be coated are those being conventionally used for the manufacture of biomedical devices, e.g. contact lenses, in particular contact lenses for extended wear, which are not hydrophilic per se. Such materials are known to the skilled artisan and may comprise for example polysiloxanes, perfluoroalkyl polyethers, fluorinated poly(meth)acrylates or equivalent fluorinated polymers derived e.g. from other polymerizable carboxylic acids, polyalkyl (meth)acrylates or equivalent alkylester polymers derived from other polymerizable carboxylic acids, or fluorinated polyolefines, such as fluorinated ethylene or propylene, for example tetrafluoroethylene, preferably in combination with specific dioxols, such as perfluoro-2,2-dimethyl-1,3-dioxol. Examples of

suitable bulk materials are e.g. Lotrafilcon A, Neofocon, Pasifocon, Telefocon, Silafocon, Fluorsilfocon, Paflufocon, Silafocon, Elastofilcon, Fluorofocon or Teflon AF materials, such as Teflon AF 1600 or Teflon AF 2400 which are copolymers of about 63 to 73 mol % of perfluoro-2,2-dimethyl-1,3-dioxol and about 37 to 27 mol % of tetrafluoroethylene, or of about 80 to 90 mol % of perfluoro-2,2-dimethyl-1,3-dioxol and about 20 to 10 mol % of tetrafluoroethylene.

Another group of preferred materials to be coated are amphiphilic segmented copolymers comprising at least one hydrophobic segment and at least one hydrophilic segment which are linked through a bond or a bridge member. Examples are silicone hydrogels, for example those disclosed in PCT applications WO 96/31792 and WO 97/49740 which are herewith incorporated by reference.

A particular preferred group of bulk materials comprises organic polymers selected from polyacrylates, polymethacrylates, polyacrylamides, poly(N,N-dimethylacrylamides), polymethacrylamides, polyvinyl acetates, polysiloxanes, perfluoroalkyl polyethers, fluorinated polyacrylates or -methacrylates and amphiphilic segmented copolymers comprising at least one hydrophobic segment, for example a polysiloxane or perfluoroalkyl polyether segment or a mixed polysiloxane/perfluoroalkyl polyether segment, and at least one hydrophilic segment, for example a polyoxazoline, poly(2-hydroxyethylmethacrylate), polyacrylamide, poly(N,N-dimethylacrylamide), polyvinylpyrrolidone polyacrylic or polymethacrylic acid segment or a copolymeric mixture of two or more of the underlying monomers.

The material to be coated may also be any blood-contacting material conventionally used for the manufacture of renal dialysis membranes, blood storage bags, pacemaker leads or vascular grafts. For example, the material to be modified on its surface may be a polyurethane, polydimethylsiloxane, polytetrafluoroethylene, polyvinylchloride, Dacron™ or Silastic™ type polymer, or a composite made therefrom.

Moreover, the material to be coated may also be an inorganic or metallic base material without suitable reactive groups, e.g. ceramic, quartz, or metals, such as silicon or gold, or other polymeric or non-polymeric substrates. E.g. for implantable biomedical applications, ceramics are very useful. In addition, e.g. for biosensor purposes, hydrophilically coated

base materials are expected to reduce nonspecific binding effects if the structure of the coating is well controlled. Biosensors may require a specific carbohydrate coating on gold, quartz, or other non-polymeric substrates.

The form of the material to be coated may vary within wide limits. Examples are particles, granules, capsules, fibres, tubes, films or membranes, preferably moldings of all kinds such as ophthalmic moldings, for example intraocular lenses, artificial cornea or in particular contact lenses.

The polyionic material being attached to the bulk material surface may consist of one single ionic polymer, for example of a polyanionic or polycationic material as described below.

Preferably, the polyionic material includes at least one bilayer, the bilayer comprising a first ionic polymer and a second ionic polymer having charges opposite of the charges of the first ionic polymer,

A suitable bilayer on the bulk material comprises a first and second ionic polymer having opposite charges, wherein "first ionic polymer" indicates the polymer that is first of all applied to the article surface, and "second ionic polymer" indicates the polymer that is applied to the article surface after it has already been modified with the first ionic polymer. The bulk material may comprise one or more than one bilayers, for example from 1 to 25 bilayers containing the same or different ionic polymers in each case, preferably from 1 to 20 bilayers, more preferably 1 to 10 bilayers, even more prefereably 1 to 5 bilayers and in particular just one bilayer.

The first ionic polymer may be cationic or anionic, preferably anionic. A suitable anionic polymer is, for example, a synthetic polymer, biopolymer or modified biopolymer comprising carboxy, sulfo, sulfato, phosphono or phosphato groups or a mixture thereof, or a salt thereof, for example a biomedical acceptable salt and especially an ophthalmically acceptable salt thereof. Anionic polymers comprising carboxy groups or a suitable salt thereof are preferred.

Examples of synthetic anionic polymers are: a linear polyacrylic acid (PAA), a branched polyacrylic acid, for example a Carbophil® or Carbopol® type from Goodrich Corp., a poly-

methacrylic acid (PMA), a polyacrylic acid or polymethacrylic acid copolymer, for example a copolymer of acrylic or methacrylic acid and a further vinylmonomer, for example acrylamide, N,N-dimethyl acrylamide or N-vinylpyrrolidone, a maleic or fumaric acid copolymer, a poly(styrenesulfonic acid) (PSS), a polyamido acid, for example a carboxy-terminated polymer of a diamine and a di- or polycarboxylic acid, for example carboxy-terminated Starburst™ PAMAM dendrimers (Aldrich), a poly(2-acrylamido-2-methylpropanesulfonic acid) (poly-(AMPS)), or an alkylene polyphosphate, alkylene polyphosphonate, carbohydrate polyphosphate or carbohydrate polyphosphonate, for example a teichoic acid.

Examples of anionic biopolymers or modified biopolymers are: hyaluronic acid, glycosaminoglycanes such as heparin or chondroitin sulfate, fucoidan, poly-aspartic acid, poly-glutamic acid, carboxymethyl cellulose, carboxymethyl dextranes, alginates, pectins, gellan, carboxyalkyl chitins, carboxymethyl chitosans, sulfated polysaccharides.

A preferred anionic polymer is a linear or branched polyacrylic acid or an acrylic acid copolymer. A more preferred anionic polymer is a linear or branched polyacrylic acid. A branched polyacrylic acid in this context is to be understood as meaning a polyacrylic acid obtainable by polymerizing acrylic acid in the presence of suitable (minor) amounts of a di- or polyvinyl compound.

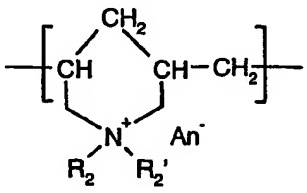
A suitable cationic polymer as part of the bilayer is, for example, a synthetic polymer, biopolymer or modified biopolymer comprising primary, secondary or tertiary amino groups or a suitable salt thereof, preferably an ophthalmically acceptable salt thereof, for example a hydrohalogenide such as a hydrochloride thereof, in the backbone or as substituents. Cationic polymers comprising primary or secondary amino groups or a salt thereof are preferred.

Examples of synthetic cationic polymers are:
(i) a polyallylamine (PAH) homo- or copolymer, optionally comprising modifier units;
(ii) a polyethyleneimine (PEI);
(iii) a polyvinylamine homo- or copolymer, optionally comprising modifier units;
(iv) a poly(vinylbenzyl-tri-C_1-C_4-alkylammonium salt), for example a poly(vinylbenzyl-trimethyl ammoniumchloride);

(v) a polymer of an aliphatic or araliphatic dihalide and an aliphatic N,N,N',N'-tetra-C_1-C_4-alkyl-alkylenediamine, for example a polymer of (a) propylene-1,3-dichloride or -dibromide or p-xylylene dichloride or dibromide and (b) N,N,N',N'-tetramethyl-1,4-tetramethylene diamine;

(vi) a poly(vinylpyridin) or poly(vinylpyridinium salt) homo- or copolymer;

(vii) a poly (N,N-diallyl-N,N-di-C_1-C_4-alkyl-ammoniumhalide) comprising units of formula



wherein R_2 and R_2' are each independently C_1-C_4-alkyl, in particular methyl, and An^- is a, for example, a halide anion such as the chloride anion;

(viii) a homo- or copolymer of a quaternized di-C_1-C_4-alkyl-aminoethyl acrylate or methacrylate, for example a poly(2-hydroxy-3-methacryloylpropyltri-C_1-C_2-alkylammonium salt) homopolymer such as a a poly(2-hydroxy-3-methacryloylpropyltri-methylammonium chloride), or a quaternized poly(2-dimethylaminoethyl methacrylate or a quaternized poly(vinylpyrrolidone-co-2-dimethylaminoethyl methacrylate);

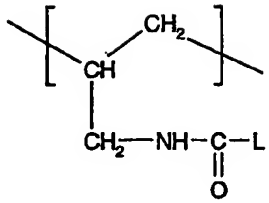
(ix) POLYQUAD® as disclosed in EP-A-456,467; or

(x) a polyaminoamide (PAMAM), for example a linear PAMAM or a PAMAM dendrimer such as a amino-terminated Starbust™ PAMAM dendrimer (Aldrich).

The above mentioned polymers comprise in each case the free amine, a suitable salt thereof, for example a biomedically acceptable salt or in particular an ophthalmically acceptable salt thereof, as well as any quaternized form, if not specified otherwise.

Suitable comonomers optionally incorporated in the polymers according to (i), (iii), (vi) or (viii) above are, for example, acrylamide, methacrylamide, N,N-dimethyl acrylamide, N-vinylpyrrolidone and the like.

Suitable modifier units of the polyallylamine (i) are, for example, of formula



(5),

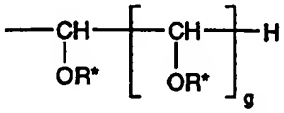
wherein L is C_2-C_6-alkyl which is substituted by two or more same or different substituents selected from the group consisting of hydroxy, C_2-C_5-alkanoyloxy and C_2-C_5-alkylamino-carbonyloxy.

L is preferably linear C_3-C_6-alkyl, more preferably linear C_4-C_5-alkyl, and most preferably n-pentyl which is in each case substituted as defined above.

Suitable substituents of the alkyl radical L are -OH, a radical -O-C(O)-R_{29} and/or a radical -O-C(O)-NH-R_{29}' wherein R_{29} and R_{29}' are each independently of the other C_1-C_4-alkyl, preferably methyl, ethyl or n- or iso-propyl, and more preferably methyl or ethyl.

Preferred substituents of the alkyl radical L are hydroxy, acetyloxy, propionyloxy, methyl-aminocarbonyloxy or ethylaminocarbonyloxy, especially hydroxy, acetyloxy or propionyloxy and in particular hydroxy.

A preferred embodiment relates to polyallyl amines comprising units of the above formula (5), wherein L is a radical of formula



(6),

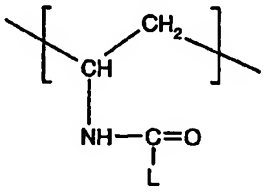
wherein g is 1, 2, 3, 4 or 5, preferably 3 or 4 and in particular 4, each R* is independently hydrogen or a radical -C(O)-R_{29} or -C(O)-NH-R_{29}', and for R_{29} and R_{29}' the above meanings and preferences apply. L is even more preferred a radical of the above formula (6) wherein g is 3 or 4, in particular 4, and each group -OR* independently is hydroxy or hydroxy which is partly or completely acetylated, in particular hydroxy. Particular preferred radicals L are 1,2,3,4,5-pentahydroxy-n-pentyl or 1,2,3,4,5-pentahydroxy-n-pentyl wherein the hydroxy groups are partly or completely acetylated.

The modified polyallylamines of the invention are derivatives of a polyallyl amine that, based on the number of amino groups of the polyallyl amine, comprise from about 1 to 99 %, preferably from 10 to 80 %, more preferably, from 15 to 75 %, even more preferably 20 to 70 % and in particular 40 to 60 %, of units of formula (5).

The term units of formula (5) or of another formula number below is always to be understood as encompassing one or more different species falling under the respective formula. Preferably the term means one single species. In addition, the polyallylamine may contain further modifier units, for example those disclosed in EP-A-1002807, formula (2a) - (2d).

A preferred polyallylamine according to the invention is a polyallylamine without modifier units or a polyallylamine having from 10 to 80 % of units of the above formula (5) based on the number of amino groups of the polyallyl amine. A particular preferred polyallylamine according to the invention is a polyallylamine without modifier units or a polyallylamine having from 15 to 75 %, based on the number of amino groups of the polyallyl amine, of units of the above formula (5) wherein L is 1,2,3,4,5-pentahydroxy-n-pentyl.

Suitable modifier units of the polyvinylamine (iii) are, for example, of formula



(5a),

wherein for L the above-given meanings and preferences apply.

A suitable polyvinylamine copolymer is, for example, a copolymer comprising vinylamine units and units derived from another hydrophilic comonomer, for example from acrylamide, N,N-dimethyl acrylamide, N-vinylpyrrolidone or the like.

Examples of cationic biopolymers or modified biopolymers are: basic peptides, proteins or glucoproteins, for example a poly-ε-lysine, albumin or collagen, aminoalkylated polysaccharides, for example a chitosan, aminodextranes.

A preferred cationic polymer forming the bilayer that is attached to the bulk material is a polyallylamine homopolymer; a polyallylamine comprising modifier units of the above formula (1); a polyvinylamine homo- or -copolymer or a polyethyleneimine homopolymer, in particular a polyallylamine or polyethyleneimine homopolymer or a poly(vinylamine-co-acrylamid) copolymer.

The molecular weight of the anionic and cationic polymers used to prepare the bilayers may vary within wide limits depending on the desired characteristics such as adhesion on the bulk material, coating thickness and the like. In general, a weight average molecular weight of from about 5000 to about 5000000, preferably from 10000 to 1000000, more preferably 15000 to 500000, even more preferably from 20000 to 200000 and in particular from 40000 to 150000, has proven as valuable both for the anionic and cationic polymer forming the bilayer.

The anionic and cationic polymers used to prepare the bilayers are in general water-soluble. The anionic and cationic polymers forming the bilayers of the invention are known and the majority of them is commercially available, or they may be prepared according to methods known in the art. Polyallylamines comprising modifier units are known, for example, from EP-A-1002807.

The formation and application of the bilayers on the bulk material surface may be accomplished according to processes known per se. For example, the bulk material is immersed in a solution of the anionic and cationic polymer, or one or more layers each of the anionic and cationic polymer are successively deposited on the modified bulk material surface, for example, by dipping, spraying, printing, spreading, pouring, rolling, spin coating or vacuum vapor deposition, spraying or particularly dipping being preferred. Following the deposition of one ionic polymer the bulk material may be rinsed or dried before the deposition of the next ionic polymer having opposite charges. However, it is preferred to omit a rinsing or drying step between the attachment of the first and second ionic polymer.

A preferred dip method involves the steps of (i) applying a coating of a first ionic polymer, for example of a cationic or preferably of an anionic polymer, to the bulk material by immersing the bulk material in a solution of the first ionic polymer; (ii) optionally, rinsing the bulk material by immersing it in a rinsing solution; (iii) optionally, drying said bulk material;

and (iv) applying a coating of a second ionic polymer having charges opposite of the charges of the first ionic polymer, for example an anionic or preferably a cationic polymer, to the bulk material by immersing the bulk material in a solution of the second ionic polymer. A more preferred dip method involves the steps of applying a coating of the first and second ionic polymer by immersing the bulk material successively in a solution each of the first and second ionic polymer without a rinsing or drying step in between. A further dip method involves immersing the bulk material in a solution comprising both the anionic and cationic polymer.

The dip solutions of the anionic and cationic polymer in general comprise the respective polymer diluted in one or more different solvents. Suitable solvents are, for example, water or an aqueous solution comprising a water-miscible organic solvent, for example a C_1-C_4-alkanol such as methanol or ethanol; the preferred solvent is pure water. The aqueous solutions of the cationic or anionic polymer advantageously each have a slightly acidic pH value, for example a pH from about 2 to about 5 and preferably from about 2.5 to about 4.5. The concentration of the dip solutions may vary within wide limits depending, for example, on the particular ionic polymer involved. However, it is generally preferred to formulate relatively dilute solutions of the ionic polymers. A preferred anionic or cationic polymer concentration is from about 0.0001 to about 0.25 weight percent, more preferably from 0.0005 to 0.15 weight percent and in particular from 0.001 to 0.1 percent by weight, relative to the total weight of the solution.

A suitable rinsing solution, if used, is preferably an aqueous solution, in particular an aqueous solution buffered at a pH of about 2 to about 7, more preferably from 2 to 5 and even more preferably from 2.5 to 4.5.

Partial drying or removal of excess rinsing solution from the surface between solution applications, if applicable, may be accomplished by a number of means known in the art. While the bulk material may be partially dried by merely allowing the lens to remain in an air atmosphere for a certain period of time, it is preferable to accelerate the drying by application of a mild stream of air to the surface. The flow rate may be adjusted as a function of the strength of the material being dried and the mechanical fixturing of the material. It should be noted that there is no requirement to completely dry the bulk material. The "partial drying" step, as used herein, refers to a removal of droplets of solution which

cling to the lens surface, rather than a desiccation of the lens. Thus, it is preferred to dry only to the extent that any water or solution film on the surface is removed.

The thickness of the coating may be adjusted by addition of one or more salts, such as sodium chloride, to the ionic polymer solution. A preferred salt concentration is about 0.1 to about 2.0 weight percent. As the salt concentration is increased, the polyelectrolyte takes on a more globular conformation. However, if the concentration is raised too high, the polyelectrolyte will not deposit well, if at all, on the lens surface. A more preferred salt concentration is about 0.7 to about 1.3 weight percent.

The bilayer formation process may be repeated a plurality of times, for example from 1 to 24 times, preferably from 1 to 14 times, more preferably from 1 to 9 times; according to one embodiment just one bilayer is deposited.
The immersion time for each of the coating and optional rinsing steps may vary depending on a number of factors. In general a rinsing time of from about 30 seconds to about 30 minutes, prefereably from 1 to 20 minutes, more preferably 1 to 10 minutes and in particular 1 to 6 minutes has proven as valuable. The immersion in the polymer solutions takes place, for example, at room temperature or at elevated temperature, preferably at room temperature, for example at a temperature of from 15 to 30°C. Following the dipping steps the bulk material may be subjected to a heat treatment in order to compact or stabilize the bilayer(s) on the bulk material surface.

Instead of coating the bulk material by means of a dip technique, said coating may also take place using spray coating techniques, wherein the above given conditions and features concerning solvents, concentrations, presence of salts, pH, temperature, number and sequence of coating steps, optional rinsing or drying steps apply accordingly. Spray coating technique in this context comprises any known process in the art including, for example, conventional techniques of applying a fluid, or techniques using ultrasonic energy, or electrostatic spray coating techniques. In addition a mixture of dip and spray techniques may also be employed.

In addition, if the polyionic material on the material surface consists of one single ionic polymer only, said ionic polymer may be applied to the surface as described above, in particular by dipping or spraying.

According to the above-mentioned methods bulk materials are obtained that comprise one polyelectrolyte or preferably one or more bilayers of polyelectrolytes adsorbed and/or heteropolarly bound on the surface. Due to this modification the surface is provided with functional groups, for example with carboxy, sulfone, sulfato, phosphono or phosphato groups or with primary, secondary or tertiary amine groups; said functional groups, preferably the carboxy groups or in particular the primary or secondary amino groups, may be further reacted with a functional initiator for radical polymerization.

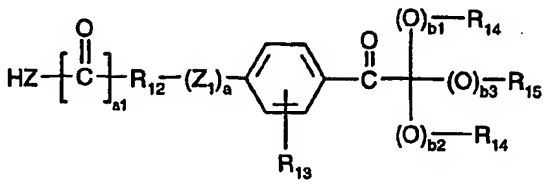
Polymerization initiators bound to the polyionic material that is attached to the bulk material surface are typically those that are initiating a radical polymerization of ethylenically unsaturated compounds. The radical polymerization may be induced thermally, or preferably by irradiation.

Suitable thermal polymerization initiators are known to the skilled artisan and comprise for example peroxides, hydroperoxides, azo-bis(alkyl- or cycloalkylnitriles), persulfates, percarbonates or mixtures thereof. An example for a functionalized thermal initiator is 4,4'-azo-bis(4-cyanovaleric acid) or derivatives thereof.

Initiators for the radiation-induced polymerization are particularly functional photoinitiators having a photoinitiator part and in addition a functional group that is coreactive with functional groups of the bilayers, particularly with amino or carboxy groups. The photoinitiator part may belong to different types, for example to the thioxanthone type and preferably to the benzoin type. Suitable functional groups that are coreactive with the bilayers attached to the surface of the bulk material are for example a carboxy, hydroxy, epoxy or particularly an isocyanato group.

Preferred polymerization initiators for use in the present invention are the photoinitiators of formulae (I) and (Ia) as disclosed in US patent No. 5,527,925, those of the formula (I) as disclosed in PCT application WO 96/20919, or those of formulae II and III including formulae IIa-IIy and IIIg as disclosed in EP-A-0281941, particularly formulae IIb, IIi, IIm, IIn, IIp, IIr, IIs, IIx and IIIg therein. The respective portion of said three documents including the definitions and preferences given for the variables in said formulae are herewith included by reference.

The polymerization initiator moieties are preferably derived from a functional photoinitiator of the formula



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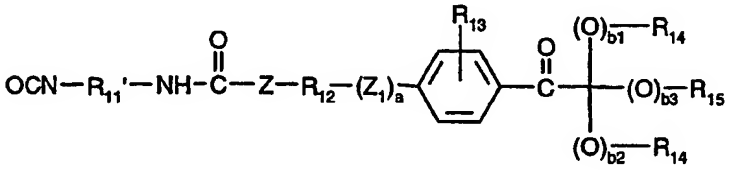
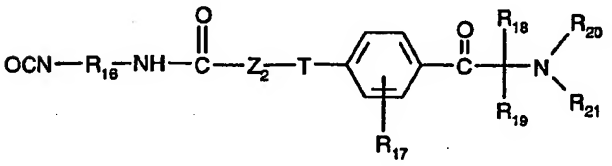
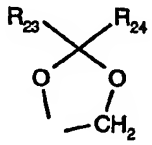


(10b), or

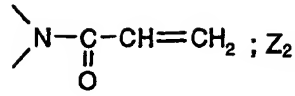


(10c),

wherein Z is bivalent -O-, -NH- or -NR_{22}-; Z_1 is -O-, -O-(O)C-, -C(O)-O- or -O-C(O)-O-; R_{13} is H, C_1-C_{12}-alkyl, C_1-C_{12}-alkoxy or N-C_1-C_{12}-alkylamino; R_{14} and R_{15} are each independently of the other H, linear or branched C_1-C_8-alkyl, C_1-C_8-hydroxyalkyl or C_6-C_{10}-aryl, or the groups R_{14}-$(O)_{b1}$- and R_{14}-$(O)_{b2}$- together are -$(CH_2)_c$- wherein c is an integer from 3 to 5, or the groups R_{14}-$(O)_{b1}$-, R_{14}-$(O)_{b2}$- and R_{15}-$(O_1)_{b3}$- together are a radical of the formula



; R_{12} is a direct bond or linear or branched C_1-C_8-alkylene that is unsubstituted or substituted by -OH and/or is uninterrupted or interrupted by one or more groups -O-, -O-C(O)- or -O-C(O)-O-; R_{11}' is branched C_3-C_{18}-alkylene, unsubstituted or C_1-C_4-alkyl- or C_1-C_4-alkoxy-substituted C_6-C_{10}-arylene, or unsubstituted or C_1-C_4-alkyl- or C_1-C_4-alkoxy-substituted C_7-C_{18}-aralkylene, unsubstituted or C_1-C_4-alkyl- or C_1-C_4-alkoxy-substituted C_3-C_8-cycloalkylene, unsubstituted or C_1-C_4-alkyl- or C_1-C_4-alkoxy-substituted C_3-C_8-cycloalkylene-C_yH_{2y}- or unsubstituted or C_1-C_4-alkyl- or C_1-C_4-alkoxy-substituted -C_yH_{2y}-(C_3-C_8-cycloalkylene)-C_yH_{2y}- wherein y is an integer from 1 to 6; R_{16} independently has the same definitions as R_{11}' or is linear C_3-C_{18}-alkylene; R_{22} is linear or branched C_1-C_6-alkyl; T

is bivalent -O-, -NH-, -S-, C_1-C_8-alkylene or  ; Z_2 is a direct bond or -O-$(CH_2)_d$- wherein d is an integer from 1 to 6 and the terminal CH_2 group of which is linked to the adjacent T in formula (10c); R_{17} is H, C_1-C_{12}-alkyl, C_1-C_{12}-alkoxy, N-C_1-C_{12}-alkylamino or -$NR_{25}R_{26}$ wherein R_{25} is C_1-C_8-alkyl and R_{26} is H or C_1-C_8-alkyl; R_{18} is linear or branched C_1-C_8-alkyl, C_2-C_8-alkenyl or C_6-C_{10}-aryl-C_1-C_8-alkyl; R_{19} independently of R_{18} has the same definitions as R_{18} or is C_6-C_{10}-aryl, or R_{18} and R_{19} together are -$(CH_2)_e$- wherein e is an integer from 2 to 6; R_{20} and R_{21} are each independently of the other linear or branched C_1-C_8-alkyl that may be substituted by C_1-C_4-alkoxy, or C_6-C_{10}-aryl-C_1-C_8-alkyl or C_2-C_8-alkenyl; or R_{20} and R_{21} together are -$(CH_2)_{f1}$-Z_3-$(CH_2)_{f2}$- wherein Z_3 is a direct bond, -O-, -S- or -NR_{26}-, and R_{26} is H or C_1-C_8-alkyl and f1 and f2 are each independently of the other an integer from 2 to 4; R_{23} and R_{24} are each independently of the other H, C_1-C_8-alkyl, C_3-C_8-cycloalkyl, benzyl or phenyl; and a, a1, b1, b2 and b3 are each independently of the other 0 or 1; subject to the provisos that b1 and b2 are each 0 when R_{15} is H; that the total of (b1+b2+b3) is not exceeding 2; and that a is 0 when R_{12} is a direct bond.

A preferred sub-group of compounds of formula (10a) or (10b) comprises those wherein, b1 and b2 are each 0; Z and Z_1 are each bivalent -O-; b3 is 0 or 1; R_{14} is C_1-C_4-alkyl or phenyl, or both groups R_{14} together are tetramethylene or pentamethylene; R_{15} is C_1-C_4-alkyl or H, R_{13} is hydrogen; a and a1 are each independently 0 or 1; R_{12} is linear or branched C_2-C_4-alkylene, or is a direct bond, in which case a is 0; R_{11}' is branched C_5-C_{10}-alkylene, phenylene or phenylene substituted by from 1 to 3 methyl groups, benzylene or benzylene substituted by from 1 to 3 methyl groups, cyclohexylene or cyclohexylene substituted by from 1 to 3 methyl groups, cyclohexyl-C_yH_{2y}- or -C_yH_{2y}-cyclohexyl-C_yH_{2y}- or cyclohexyl-C_yH_{2y}- or -C_yH_{2y}-cyclohexyl-C_yH_{2y}- substituted by from 1 to 3 methyl groups; y is 1 or 2; and R_{16} has the same definitions as R_{11}' or is linear C_3-C_{10}alkylene.

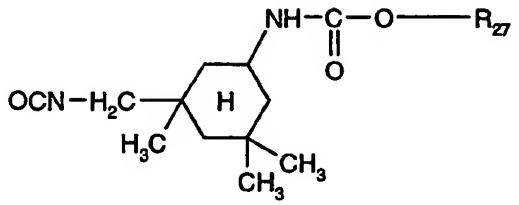
An especially preferred sub-group of compounds of formula (10a) or (10b) comprises those wherein, b1 and b2 are each 0, Z and Z_1 are each bivalent -O-, b3 is 0 or 1; R_{14} is methyl or phenyl, or both groups R_{14} together are pentamethylene; R_{15} is methyl or H; R_{13} is hydrogen; a is 1 and R_{12} is ethylene, or a is 0 and R_{12} is a direct bond; a1 is 0 or 1; R_{11}' is branched C_6-C_{10}-alkylene, phenylene or phenylene substituted by from 1 to 3 methyl groups, benzylene or benzylene substituted by from 1 to 3 methyl groups, cyclohexylene or

cyclohexylene substituted by from 1 to 3 methyl groups, cyclohexyl-CH_2- or cyclohexyl-CH_2- substituted by from 1 to 3 methyl groups; R_{16} has the same definitions as R_{11}' or is linear C_5-C_{10}alkylene.

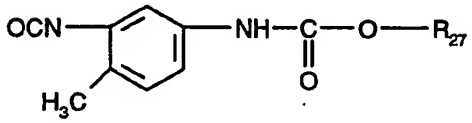
A preferred sub-group of compounds of formula (10c) comprises those wherein T is bivalent -O-, -NH-, -S- or -$(CH_2)_y$- wherein y is an integer from 1 to 6; Z_2 is a direct bond or -O-$(CH_2)_y$- wherein y is an integer from 1 to 6 and the terminal CH_2 group of which is linked to the adjacent T in formula (10c); R_{17} is H, C_1-C_{12}-alkyl or C_1-C_{12}-alkoxy; R_{18} is linear C_1-C_8-alkyl, C_2-C_8-alkenyl or C_6-C_{10}-aryl-C_1-C_8-alkyl; R_{19} independently of R_{18} has the same definitions as R_{18} or is C_6-C_{10}-aryl, or R_{18} and R_{19} together are -$(CH_2)_e$- wherein e is an integer from 2 to 6; R_{20} and R_{21} are each independently of the other linear or branched C_1-C_8-alkyl that may be substituted by C_1-C_4-alkoxy, or C_6-C_{10}-aryl-C_1-C_8-alkyl or C_2-C_8-alkenyl; or R_{20} and R_{21} together are -$(CH_2)_{f1}$-Z_3-$(CH_2)_{f2}$- wherein Z_3 is a direct bond, -O-, -S- or -NR_{26}-, and R_{26} is H or C_1-C_8-alkyl and f1 and f2 are each independently of the other an integer from 2 to 4; and R_{16} is branched C_6-C_{10}-alkylene, phenylene or phenylene substituted by from 1 to 3 methyl groups, benzylene or benzylene substituted by from 1 to 3 methyl groups, cyclohexylene or cyclohexylene substituted by from 1 to 3 methyl groups, cyclohexylene-CH_2- or cyclohexylene-CH_2- substituted by from 1 to 3 methyl groups.

An especially preferred sub-group of compounds of formula (10c) comprises those wherein T is bivalent -O-; Z_2 is -O-$(CH_2)_y$- wherein y is an integer from 1 to 4 and the terminal CH_2 group of which is linked to the adjacent T in formula (10c); R_{17} is H; R_{18} is methyl, allyl, tolylmethyl or benzyl, R_{19} is methyl, ethyl, benzyl or phenyl, or R_{18} and R_{19} together are pentamethylene, R_{20} and R_{21} are each independently of the other C_1-C_4-alkyl or R_{20} and R_{21} together are -$CH_2CH_2OCH_2CH_2$-, and R_{16} is branched C_6-C_{10}-alkylene, phenylene or phenylene substituted by from 1 to 3 methyl groups, benzylene or benzylene substituted by from 1 to 3 methyl groups, cyclohexylene or cyclohexylene substituted by from 1 to 3 methyl groups, cyclohexylene-CH_2- or cyclohexylene-CH_2- substituted by from 1 to 3 methyl groups.

Some examples of especially preferred functional photoinitiators are the compounds of formulae



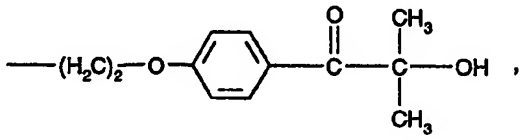
(11a),



(11b), or

(11c),

wherein R_{27} is a radical



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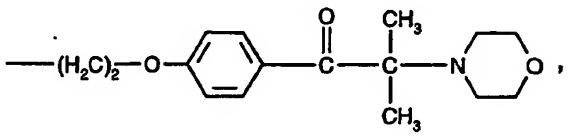

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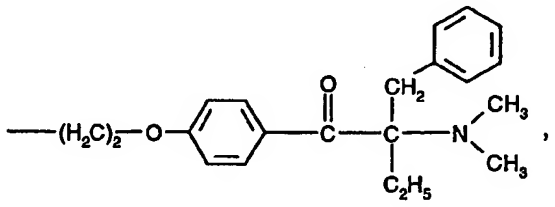
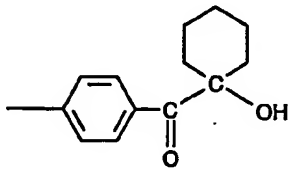


, or

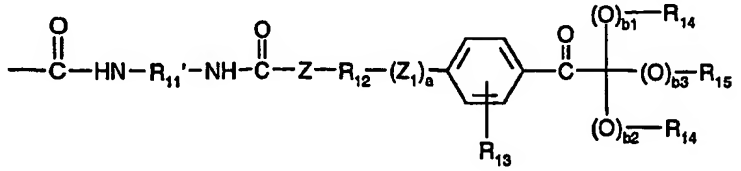


.

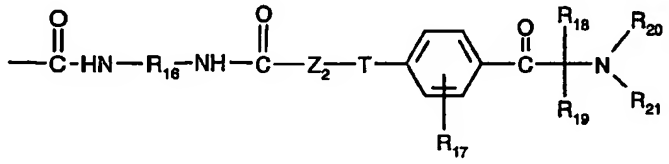
In a preferred embodiment of the invention, the covalent bonding between the bilayer(s) that is/are attached to the bulk material surface and the photoinitiator occurs via reaction of an amino or carboxy group, particularly an amino group, of the modified bulk material surface with an isocyanato group of the photoinitiator, for example using a photoinitiator of the above formula (10b), (10c), (11a), (11b) or (11c). Suitable methods for this are known, for example, from the above-mentioned documents. The reaction may be carried out, for

example, at elevated temperature, for example from 0° to 100°C and preferably at room temperature, and optionally in the presence of a catalyst. After the reaction, excess compounds can be removed, for example, with solvents.

According to a preferred embodiment of the invention the bulk material comprises on its modified surface $-NH_2$ and/or -NH- groups, that are coreactive with isocyanato groups, some of whose H atoms have been substituted by radicals of the formulae



(12a) or



(12b),

wherein for the variables R_{11}'-R_{21}, T, Z, Z_1, Z_2, a, b1, b2 and b3 the above-given meanings and preferences apply.

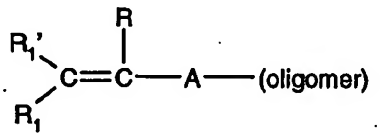
In another embodiment of the invention, the covalent bonding between the modified bulk material surface and the photoinitiator occurs via reaction of a carboxy or isocyanato group of the bilayer attached to the bulk material with a hydroxy, amino or alkylamino group of the photoinitiator, for example using a photoinitiator of the above formula (10a). Isocyanato groups may be attached to the bilayer, for example, by first reacting an above-mentioned modified bulk material containing a bilayer with amino groups on the surface, selectively with one isocyanato group of a diisocyanate of formula OCN-R_{11}'-NCO, wherein R_{11}' has the above-given meanings; the thus modified bulk material then may be reacted with a photo-initiator of the above-mentioned formula (10a). The reaction of carboxy groups of the bilayer with hydroxy or amino groups of the photoinitiator of formula (10a) is well-known in the art and may be carried out, for example, as described in textbooks of organic chemistry.

A hydrophilic monomer useful to provide the hydrophilic surface coating (b) on the initiator-modified bulk material surface is typical a monomer that yields as homopolymer a polymer that is water-soluble or can absorb at least 10 % by weight of water. Examples of preferred

hydrophilic monomers are hydroxy-substituted C_2-C_4-alkyl acrylates and methacrylates, acrylamide, methacrylamide, N,N-di-C_1-C_4-alkyl acrylamides and methacrylamides, ethoxylated acrylates and methacrylates, hydroxy-substituted C_2-C_4-alkyl acrylamides and methacrylamides, hydroxy-substituted C_1-C_4-alkyl vinyl ethers, sodium ethylenesulfonate, sodium styrenesulfonate, 2-acrylamido-2-methylpropanesulfonic acid, N-vinylpyrrole, N-vinylsuccinimide, N-vinylpyrrolidone, 2- or 4-vinylpyridine, acrylic acid, methacrylic acid, amino- (the term "amino" also including quaternary ammonium), mono-C_1-C_4-alkylamino- or di-C_1-C_4-alkylamino-C_1-C_4-alkyl acrylates and methacrylates, allylalcohol and the like. Hydroxy-substituted or N,N-di-C_1-C_2-alkylamino-substituted C_2-C_4alkyl(meth)acrylates, five- to seven-membered N-vinyl lactams, N,N-di-C_1-C_4alkyl(meth)acrylamides and vinylically unsaturated carboxylic acids having a total of from 3 to 5 carbon atoms, for example, are preferred.

Examples of preferred hydrophilic vinylic monomers include hydroxyethyl methacrylate, hydroxyethyl acrylate, acrylamide, methacrylamide, N,N-dimethylacrylamide, allyl alcohol, N-vinylpyrrolidone, acrylic acid, methacrylic acid and N,N-dimethylaminoethyl methacrylate.

Preferably the hydrophilic surface coating (b) on the bulk material (a) is obtained using a suitable macromonomer. A preferred macromonomer is, for example, of formula

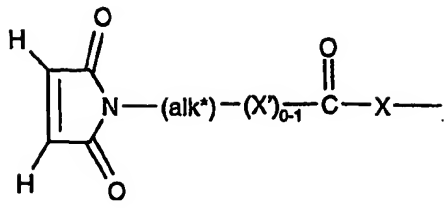


(1),

wherein R_1 is hydrogen, C_1-C_6-alkyl or a radical -COOR';
R, R' and R_1' are each independently of the other hydrogen or C_1-C_6-alkyl;
A is a direct bond or is a radical of formula

$-C(O)-(A_1)_n-X-$ (2a) or
$-(A_2)_m-NH-C(O)-X-$ (2b); or
$-(A_2)_m-X-C(O)-$ (2c); or
$-C(O)-NH-C(O)-X-$ (2d); or
$-C(O)-X_1-(alk^*)-X-C(O)-$ (2e); or

A and R_1, together with the adjacent double bond, are a radical of formula



(2f),

A_1 is -O-C_2-C_{12}-alkylene which is unsubstituted or substituted by hydroxy, or is -O-C_2-C_{12}-alkylene-NH-C(O)- or -O-C_2-C_{12}-alkylene-O-C(O)-NH-R_{11}-NH-C(O)-, wherein R_{11} is linear or branched C_1-C_{18}-alkylene or unsubstituted or C_1-C_4-alkyl- or C_1-C_4-alkoxy-substituted C_6-C_{10}-arylene, C_7-C_{18}-aralkylene, C_6-C_{10}-arylene-C_1-C_2-alkylene-C_6-C_{10}-arylene, C_3-C_8-cycloalkylene, C_3-C_8-cycloalkylene-C_1-C_6-alkylene, C_3-C_8-cycloalkylene-C_1-C_2-alkylene-C_3-C_8-cycloalkylene or C_1-C_6-alkylene-C_3-C_8-cycloalkylene-C_1-C_6-alkylene ;

A_2 is C_1-C_8-alkylene; phenylene or benzylene;

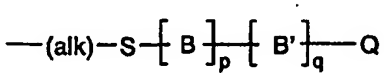
m and n are each independently of the other the number 0 or 1;

X, X_1 and X' are each independently of the other a bivalent group -O- or -NR"-, wherein R" is hydrogen or C_1-C_6-alkyl;

(alk*) is C_2-C_{12}-alkylene;

and (oligomer) denotes

(i) the radical of a telomer of formula



(3a),

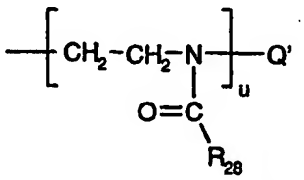
wherein (alk) is C_2-C_{12}-alkylene,

Q is a monovalent group that is suitable to act as a polymerization chain-reaction terminator,

p and q are each independently of another an integer from 0 to 250, wherein the total of (p+q) is an integer from 2 to 250,

and B and B' are each independently of the other a 1,2-ethylene radical derivable from a copolymerizable vinyl monomer by replacing the vinylic double bond by a single bond, at least one of the radicals B and B' being substituted by a hydrophilic substituent; or

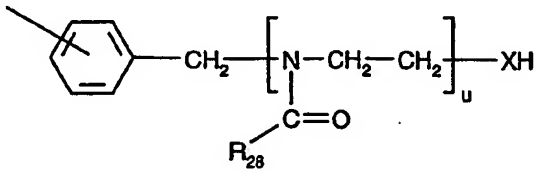
(ii) the radical of an oligomer of the formula



(3b),

wherein R_{28} is hydrogen or unsubstituted or hydroxy-substituted C_1-C_{12}-alkyl, u is an integer from 2 to 250 and Q' is a radical of a polymerization initiator; or

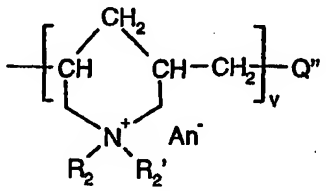
(iii) the radical of formula



(3b'),

wherein R_{28}, X and u are as defined above, or

(iv) the radical of an oligomer of formula



(3c),

wherein R_2 and R_2' are each independently C_1-C_4-alkyl, An^- is an anion, v is an integer from 2 to 250, and Q" is a monovalent group that is suitable to act as a polymerization chain-reaction terminator; or

(v) the radical of an oligopeptide of formula

$$-(CHR_4\text{-}C(O)\text{-}NH)_t\text{-}CHR_4\text{-}COOH \quad \text{(3d) or}$$

$$-CHR_4\text{-}(NH\text{-}C(O)\text{-}CHR_4)_t\text{-}NH_2 \quad \text{(3d')},$$

wherein R_4 is hydrogen or C_1-C_4-alkyl which is unsubstituted or substituted by hydroxy, carboxy, carbamoyl, amino, phenyl, o-, m- or p-hydroxyphenyl, imidazolyl, indolyl or a radical -NH-C(=NH)-NH_2 and t is an integer from 2 to 250, or the radical of an oligopeptide based on proline or hydroxyproline; or

(vi) the radical of a polyalkylene oxide of formula

$$-(alk^{\cdot\cdot}\text{-}O)_z\text{-}[CH_2\text{-}CH_2\text{-}O]_r\text{-}[CH_2\text{-}CH(CH_3)\text{-}O]_s\text{-}R_{30} \quad \text{(3e)},$$

wherein R_{30} is hydrogen or C_1-C_{24}-alkyl, ($alk^{\cdot\cdot}$) is C_2-C_4-alkylene, z is 0 or 1, r and s are each independently an integer from 0 to 250 and the total of (r+s) is from 2 to 250; or

(vii) the radical of an oligosaccharide;

subject to the provisos that

A is not a direct bond if (oligomer) is a radical of formula (3a);

A is a direct bond if (oligomer) is a radical of formula (3b');

A is not a radical of formula (2c) or (2e) if (oligomer) is a radical of formula (3b), (3c), (3d), (3e) or is the radical of an oligosaccharide;and
A is a radical of formula (2c) or (2e) if (oligomer) is a radical of formula (3d').

The following preferences apply to the variables contained in the definition of the macromonomer of formula (1):
R' is preferably hydrogen or C_1-C_4-alkyl, more preferably hydrogen or C_1-C_2-alkyl and particularly preferably hydrogen.
R_1 is preferably hydrogen, methyl or carboxyl, and particularly preferably hydrogen.
R is preferably hydrogen or methyl.
X is preferably a bivalent group -O- or -NH-. X is particularly preferably the group -NH- if (oligomer) is a radical of formula (3a); (3c) or (3d), and is particularly preferably the group -O- if (oligomer) is a radical of formula (3b). X' is preferably -O- or -NH- and more preferably -NH-. X_1 is preferably -O- or -NH-.
R_{11} as alkylene is preferably a linear or branched C_3-C_{14}alkylene radical, more preferably a linear or branched C_4-C_{12}alkylene radical and most preferably a linear or branched C_6-C_{10}-alkylene radical.

When R_{11} is arylene, it is, for example, naphthylene or especially phenylene, each of which may be substituted, for example, by C_1-C_4-alkyl or by C_1-C_4-alkoxy. Preferably, R_{11} as arylene is 1,3- or 1,4-phenylene that is unsubstituted or substituted by C_1-C_4-alkyl or by C_1-C_4-alkoxy in the ortho-position to at least one linkage site. Examples of substituted arylene are 1-methyl-2,4-phenylene, 1,5-dimethyl-2,4-phenylene, 1-methoxy-2,4-phenylene and 1-methyl-2,7-naphthylene.

R_{11} as aralkylene is preferably naphthylalkylene and most preferably phenylalkylene. The alkylene group in aralkylene contains preferably from 1 to 12, more preferably from 1 to 6 and most preferably from 1 to 4 carbon atoms. Most preferably, the alkylene group in aralkylene is methylene or ethylene.

When R_{11} is cycloalkylene, it is preferably C_5-C_6cycloalkylene and most preferably cyclohexylene that is unsubstituted or substituted by methyl.

When R_{11} is cycloalkylene-alkylene, it is preferably cyclopentylene-C_1-C_4-alkylene and espe-

cially cyclohexylene-C_1-C_4-alkylene, each unsubstituted or mono- or poly-substituted by C_1-C_4-alkyl, especially methyl. More preferably, the group cycloalkylene-alkylene is cyclohexylene-ethylene and, most preferably, cyclohexylene-methylene, each unsubstituted or substituted in the cyclohexylene radical by from 1 to 3 methyl groups.

When R_{11} is alkylene-cycloalkylene-alkylene, it is preferably C_1-C_4-alkylene-cyclopentylene-C_1-C_4-alkylene and especially C_1-C_4-alkylene-cyclohexylene-C_1-C_4-alkylene, each unsubstituted or mono- or poly-substituted by C_1-C_4-alkyl, especially methyl. More preferably, the group alkylene-cycloalkylene-alkylene is ethylene-cyclohexylene-ethylene and, most preferably, is methylene-cyclohexylene-methylene, each unsubstituted or substituted in the cyclohexylene radical by from 1 to 3 methyl groups.

R_{11} as C_3-C_8-cycloalkylene-C_1-C_2-alkylene-C_3-C_8-cycloalkylene or C_6-C_{10}-arylene-C_1-C_2-alkylene-C_6-C_{10}-arylene is preferably C_5-C_6-cycloalkylene-methylene-C_5-C_6-cycloalkylene or phenylene-methylene-phenylene, each of which may be unsubstituted or substituted in the cycloalkyl or phenyl ring by one or more methyl groups.

The radical R_{11} has a symmetrical or, preferably, an asymmetrical structure. A preferred group of radicals R_{11} comprises those, wherein R_{11} is linear or branched C_6-C_{10}alkylene; cyclohexylene-methylene or cyclohexylene-methylene-cyclohexylene each unsubstituted or substituted in the cyclohexyl moiety by from 1 to 3 methyl groups; or phenylene or phenylene-methylene-phenylene each unsubstituted or substituted in the phenyl moiety by methyl. The bivalent radical R_{11} is derived preferably from a diisocyanate and most preferably from a diisocyanate selected from the group isophorone diisocyanate (IPDI), toluylene-2,4-diisocyanate (TDI), 4,4'-methylenebis(cyclohexyl isocyanate), 1,6-diisocyanato-2,2,4-trimethyl-n-hexane (TMDI), methylenebis(phenyl isocyanate), methylenebis(cyclohexyl-4-isocyanate) and hexamethylene diisocyanate (HMDI).

Preferred meanings of A_1 are unsubstituted or hydroxy-substituted -O-C_2-C_8-alkylene or a radical -O-C_2-C_6-alkylene-NH-C(O)- and particularly -O-$(CH_2)_{2-4}$-, -O-CH_2-CH(OH)-CH_2- or a radical -O-$(CH_2)_{2-4}$-NH-C(O)-. A particularly preferred meaning of A_1 is the radical -O-$(CH_2)_2$-NH-C(O)-.

A_2 is preferably C_1-C_6-alkylene, phenylene or benzylene, more preferably C_1-C_4-alkylene and even more preferably C_1-C_2-alkylene.
n is an integer of 0 or preferably 1. m is preferably an integer of 1.
R_1' is preferably hydrogen or methyl and particularly preferably hydrogen.
In case that (oligomer) is a radical of formula (3a), (3b), (3c), (3d), (3e) or is the radical of an oligosaccharide. A preferably denotes a radical of formula (2a) or (2b) and particularly preferably a radical of formula (2a), wherein the above given meanings and preferences apply for the variables contained therein.
A preferred group of hydrophilic macromonomers according to the invention comprises compounds of the above formula (1), wherein R is hydrogen or methyl, R_1 is hydrogen, methyl or carboxyl, R_1' is hydrogen, A is a radical of the formula (2a) or (2b) and (oligomer) is a radical of formula (3a), (3b), (3c), (3d), (3e) or is the radical of an oligosaccharide . An even more preferred group of hydrophilic macromonomers comprises compounds of the above formula (1), wherein R is hydrogen or methyl, R_1 and R_1' are each hydrogen, A is a radical of the formula (2a) and (oligomer) is a radical of formula (3a). A further group of preferred macromonomers comprises compounds of formula (1), wherein A is a radical of formula (2e) above and (oligomer) is a radical of formula (3a).

(alk) and (alk*) are each independently preferably C_2-C_8-alkylene, more preferably C_2-C_6-alkylene, even more preferably C_2-C_4-alkylene and particularly preferably 1,2-ethylene. The alkylene radicals (alk) and (alk*) may be branched or preferably linear alkylene radicals.

Q is for example hydrogen.

The total of (p+q) is preferably an integer from 2 to 150, more preferably from 5 to 100, even more preferably from 5 to 75 and particularly preferably from 10 to 50. In a preferred embodiment of the invention q is 0 and p is an integer from 2 to 250, preferably from 2 to 150, more preferably from 5 to 100, even more preferably from 5 to 75 and particularly preferably from 10 to 50. In a further preferred embodiment p is from 4 to 99, q is from 1 to 96 and the total of (p+q) is from 5 to 100.

Suitable hydrophilic substituents of the radicals B or B' may be non-ionic, anionic, cationic or zwitterionic substituents. Accordingly, the telomer chain of formula (3a) that contains monomer units B and/or B' may be a charged chain containing anionic, cationic and/or

zwitterionic groups or may be an uncharged chain. In addition, the telomer chain may comprise a copolymeric mixture of uncharged and charged units. The distribution of the charges within the telomer, if present, may be random or blockwise.

In one preferred embodiment of the invention, the telomer radical of formula (3a) is composed solely of non-ionic monomer units B and/or B'. In another preferred embodiment of the invention, the telomer radical of formula (3a) is composed solely of ionic monomer units B and/or B', for example solely of cationic monomer units or solely of anionic monomer units. Still another preferred embodiment of the invention is directed to telomer radicals of formula (3a) comprising nonionic units B and ionic units B'.

Suitable non-ionic substituents of B or B' include for example a radical C_1-C_6-alkyl which is substituted by one or more same or different substituents selected from the group consisting of -OH, C_1-C_4-alkoxy and -NR_9R_9', wherein R_9 and R_9' are each independently of another hydrogen or unsubstituted or hydroxy-substituted C_1-C_6-alkyl or phenyl; phenyl which is substituted by hydroxy, C_1-C_4-alkoxy or -NR_9R_9', wherein R_9 and R_9' are as defined above; a radical -COOY, wherein Y is C_1-C_{24}-alkyl which is unsubstituted or substituted, for example, by hydroxy, C_1-C_4-alkoxy, -O-$Si(CH_3)_3$, -NR_9R_9' wherein R_9 and R_9' are as defined above, a radical -O-$(CH_2CH_2O)_{1-24}$-E wherein E is hydrogen or C_1-C_6-alkyl, or a radical -NH-C(O)-O-G, wherein -O-G is the radical of a saccharide with 1 to 8 sugar units or is a radical -O-$(CH_2CH_2O)_{1-24}$-E, wherein E is as defined above, or Y is C_5-C_8-cycloalkyl which is unsubstituted or substituted by C_1-C_4-alkyl or C_1-C_4-alkoxy, or is unsubstituted or C_1-C_4-alkyl- or C_1-C_4-alkoxy-substituted phenyl or C_7-C_{12}-aralkyl; -$CONY_1Y_2$ wherein Y_1 and Y_2 are each independently hydrogen, C_1-C_{12}-alkyl, which is unsubstituted or substituted for example by hydroxy, C_1-C_4-alkoxy or a radical -O-$(CH_2CH_2O)_{1-24}$-E wherein E is as defined above, or Y_1 and Y_2 together with the adjacent N-atom form a five- or six-membered heterocyclic ring having no additional heteroatom or one additional oxygen or nitrogen atom; a radical -OY_3, wherein Y_3 is hydrogen; or C_1-C_{12}-alkyl which is unsubstituted or substituted by -NR_9R_9'; or is a radical -C(O)-C_1-C_4-alkyl; and wherein R_9 and R_9' are as defined above; or a five- to seven-membered heterocyclic radical having at least one N-atom and being bound in each case via said nitrogen atom.

Suitable anionic substituents of B or B' include for example C_1-C_6-alkyl which is substituted by -SO_3H, -OSO_3H, -OPO_3H_2 and -COOH; phenyl which is substituted by one or more same

or different substituents selected from the group consisting of $-SO_3H$, -COOH, -OH and $-CH_2-SO_3H$; -COOH; a radical $-COOY_4$, wherein Y_4 is C_1-C_{24}-alkyl which is substituted for example by -COOH, $-SO_3H$, $-OSO_3H$, $-OPO_3H_2$ or by a radical -NH-C(O)-O-G' wherein G' is the radical of an anionic carbohydrate; a radical $-CONY_5Y_6$ wherein Y_5 is C_1-C_{24}-alkyl which is substituted by -COOH, $-SO_3H$, $-OSO_3H$, or $-OPO_3H_2$ and Y_6 independently has the meaning of Y_5 or is hydrogen or C_1-C_{12}-alkyl; or $-SO_3H$; or a salt thereof, for example a sodium, potassium, ammonium or the like salt thereof.

Suitable cationic substituents of B or B' include C_1-C_{12}-alkyl which is substituted by a radical $-NR_9R_9'R_9''^+An^-$, wherein R_9, R_9' and R_9'' are each independently of another hydrogen or unsubstituted or hydroxy-substituted C_1-C_6-alkyl or phenyl, and An^- is an anion; or a radical $-C(O)OY_7$, wherein Y_7 is C_1-C_{24}-alkyl which is substituted by $-NR_9R_9'R_9''^+An^-$ and is further unsubstituted or substituted for example by hydroxy, wherein R_9, R_9', R_9'' and An^- are as defined above.

Suitable zwitterionic substituents of B or B' include a radical $-R_3-Zw$, wherein R_3 is a direct bond or a functional group, for example a carbonyl, carbonate, amide, ester, dicarboanhydride, dicarboimide, urea or urethane group; and Zw is an aliphatic moiety comprising one anionic and one cationic group each.

The following preferences apply to the hydrophilic substituents of B and B':
(i) non-ionic substituents:
Preferred alkyl substituents of B or B' are C_1-C_4-alkyl, in particular C_1-C_2-alkyl, which is substituted by one or more substituents selected from the group consisting of -OH and $-NR_9R_9'$, wherein R_9 and R_9' are each independently of another hydrogen or C_1-C_4-alkyl, preferably hydrogen, methyl or ethyl and particularly preferably hydrogen or methyl, for example $-CH_2-NH_2$, $-CH_2-N(CH_3)_2$.
Preferred phenyl substituents of B or B' are phenyl which is substituted by $-NH_2$ or $N(C_1$-C_2-alkyl$)_2$, for example o-, m- or p-aminophenyl.
In case that the hydrophilic substituent of B or B' is a radical -COOY, Y as optionally substituted alkyl is preferably C_1-C_{12}-alkyl, more preferably C_1-C_6-alkyl, even more preferably C_1-C_4-alkyl and particularly preferably C_1-C_2-alkyl, each of which being unsubstituted or substituted as mentioned above. In case that the alkyl radical Y is substituted by $-NR_9R_9'$, the above-given meanings and preferences apply for R_9 and R_9'.

Examples of suitable saccharide substituents -O-G of the alkyl radical Y that is substituted by -NH-C(O)-O-G are the radical of a mono- or disaccharide, for example glucose, acetyl glucose, methyl glucose, glucosamine, N-acetyl glucosamine, glucono lactone, mannose, galactose, galactosamine, N-acetyl galactosamine, fructose, maltose, lactose, fucose, saccharose or trehalose, the radical of an anhydrosaccharide such as levoglucosan, the radical of a glucosid such as octylglucosid, the radical of a sugar alcohol such as sorbitol, the radical of a sugar acid derivative such as lactobionic acid amide, or the radical of an oligosaccharide with a maximum of 8 sugar units, for example fragments of a cyclodextrin, starch, chitosan, maltotriose or maltohexaose. The radical -O-G preferably denotes the radical of a mono- or disaccharide or the radical of a cyclodextrin fragment with a maximum of 8 sugar units. Particular preferred saccharide radicals -O-G are the radical of trehalose or the radical of a cyclodextrin fragment. In case that the alkyl radical Y is substituted by a radical $-O-(CH_2CH_2O)_{1-24}-E$ or -NH-C(O)-O-G wherein -O-G is $-O-(CH_2CH_2O)_{1-24}-E$, the number of (CH_2CH_2O) units is preferably from 1 to 12 in each case and more preferably from 2 to 8. E is preferably hydrogen or C_1-C_2-alkyl.
Y as C_5-C_8-cycloalkyl is for example cyclopentyl or preferably cyclohexyl, each of which being unsubstituted or substituted for example by 1 to 3 C_1-C_2-alkyl groups.Y as C_7-C_{12}-aralkyl is for example benzyl.

Preferred nonionic radicals -COOY are those wherein Y is C_1-C_4-alkyl; or C_2-C_4-alkyl which is substituted by one or two substituents selected from the group consisting of hydroxy; ; C_1-C_2-alkoxy; $-O-Si(CH_3)_3$; and $-NR_9R_9'$ wherein R_9 and R_9' are each independently of another hydrogen or C_1-C_4-alkyl; or Y is a radical $-CH_2CH_2-O-(CH_2CH_2O)_{1-12}-E$ wherein E is hydrogen or C_1-C_2-alkyl; or is a radical -C_2-C_4-alkylene-NH-C(O)-O-G, wherein -O-G is the radical of a saccharide.

More preferred non-ionic radicals -COOY are those wherein Y is C_1-C_2-alkyl, particularly methyl; or C_2-C_4-alkyl which is substituted by one or two substituents selected from the group consisting of -OH and $-NR_9R_9'$ wherein R_9 and R_9' are each independently of another hydrogen or C_1-C_2-alkyl; or a radical $-CH_2CH_2-O-(CH_2CH_2O)_{1-12}-E$ wherein E is hydrogen or C_1-C_2-alkyl; or is a radical -C_2-C_4-alkylene-NH-C(O)-O-G wherein -O-G is the radical of a saccharide.

Particularly preferred radicals -COOY comprise those wherein Y is C_2-C_3-alkyl, which is substituted by hydroxy or N,N-di-C_1-C_2-alkylamino, or is a radical -C_2-C_3-alkylene-NH-C(O)-O-G wherein -O-G is the radical of trehalose.

Preferred non-ionic substituents -C(O)-NY_1Y_2 of B or B' are those wherein Y_1 and Y_2 are each independently of the other hydrogen or C_1-C_4-alkyl which is unsubstituted or substituted by hydroxy; or Y_1 and Y_2 together with the adjacent N-atom form a heterocyclic 6-membered ring having no further heteroatom or having one further N- or O-atom. Even more preferred meanings of Y_1 and Y_2, independently of each other, are hydrogen or C_1-C_2-alkyl which is unsubstituted or substituted by hydroxy; or Y_1 and Y_2 together with the adjacent N-atom form a N-C_1-C_2-alkylpiperazino or morpholino ring. Particularly preferred non-ionic radicals -C(O)-NY_1Y_2 are those wherein Y_1 and Y_2 are each independently of the other hydrogen or C_1-C_2-alkyl; or Y_1 and Y_2 together with the adjacent N-atom form a morpholino ring.

Preferred non-ionic substituents -OY_3 of B or B' are those wherein Y_3 is hydrogen, C_1-C_4-alkyl which is unsubstituted or substituted by -NH_2 or -N(C_1-C_2-alkyl)$_2$, or is a group -C(O)C_1-C_2-alkyl. Y_3 is particularly preferred hydrogen or acetyl.

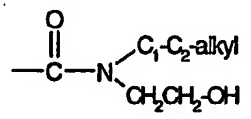
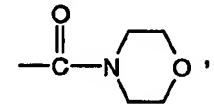
Preferred non-ionic heterocyclic substituents of B or B' are a 5- or 6-membered heteroaromatic or heteroaliphatic radical having one N-atom and in addition no further heteroatom or an additional N- or O- heteroatom, or is a 5 to 7-membered lactame. Examples of such heterocyclic radicals are N-pyrrolidonyl, 2- or 4-pyridinyl, 2-methyl pyridin-5-yl, 2-, 3- oder 4-hydroxypyridinyl, N-ε-caprolactamyl, N-imidazolyl, 2-methylimidazol-1-yl, N-morpholinyl or 4-N-methylpiperazin-1-yl, particularly N-morpholinyl or N-pyrrolidonyl.

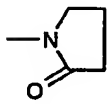
A group of preferred non-ionic substituents of B or B' comprises C_1-C_2-alkyl, which is unsubstituted or substituted by -OH or -NR_9R_9', wherein R_9 and R_9' are each independently of the other hydrogen or C_1-C_2-alkyl; a radical -COOY wherein Y is C_1-C_4-alkyl; C_2-C_4-alkyl which is substituted by -OH or -NR_9R_9' wherein R_9 and R_9' are each independently of another hydrogen or C_1-C_2-alkyl, or Y is a radical -C_2-C_4-alkylene-NH-C(O)-O-G wherein -O-G is the radical of a saccharide; a radical -C(O)-NY_1Y_2, wherein Y_1 and Y_2 are each independently of the other hydrogen or C_1-C_4-alkyl which is unsubstituted or substituted by hydroxy, or Y_1 and Y_2 together with the adjacent N-atom form a heterocyclic 6-membered

ring having no further heteroatom or having one further N- or O-atom; a radical -OY_3, wherein Y_3 is hydrogen, C_1-C_4-alkyl which is unsubstituted or substituted by -NH_2 or -$N(C_1$-C_2-alkyl$)_2$, or is a group -$C(O)C_1$-C_2-alkyl; or a 5- or 6-membered heteroaromatic or heteroaliphatic radical having one N-atom and in addition no further heteroatom or an additional N-, O- or S-heteroatom, or a 5 to 7-membered lactame.

A group of more preferred non-ionic substituents of B or B' comprises a radical -COOY, wherein Y is C_1-C_2-alkyl, C_2-C_3-alkyl, which is substituted by hydroxy, amino or N,N-di-C_1-C_2-alkylamino, or is a radical -C_2-C_4-alkylene-NH-C(O)-O-G wherein -O-G is the radical of trehalose; a radical -CO-NY_1Y_2, wherein Y_1 and Y_2 are each independently of the other hydrogen or C_1-C_2-alkyl which is unsubstituted or substituted by hydroxy, or Y_1 and Y_2 together with the adjacent N-atom form a N-C_1-C_2-alkylpiperazino or morpholino ring; or a heterocyclic radical selected from the group consisting of N-pyrrolidonyl, 2- or 4-pyridinyl, 2-methylpyridin-5-yl, 2-, 3- oder 4-hydroxypyridinyl, N-ε-caprolactamyl, N-imidazolyl, 2-methylimidazol-1-yl, N-morpholinyl and 4-N-methylpiperazin-1-yl.

A particularly preferred group of non-ionic substituents of B or B' comprises the radicals

-$CONH_2$, -$CON(CH_3)_2$, -$CONH$-$(CH_2)_2$-OH,  ,  ,

 , -COO-$(CH_2)_2$-$N(CH_3)_2$, and -$COO(CH_2)_{2\text{-}4}$-NHC(O)-O-G whereln -O-G is the radical of trehalose.

(ii) anionic substituents:

Preferred anionic substituents of B or B' are C_1-C_4-alkyl, in particular C_1-C_2-alkyl, which is substituted by one or more substituents selected from the group consisting of -SO_3H and -OPO_3H_2, for example -CH_2-SO_3H; phenyl which is substituted by -SO_3H or sulfomethyl, for example o-, m- or p-sulfophenyl or o-, m- or p-sulfomethylphenyl; -COOH; a radical -$COOY_4$, wherein Y_4 is C_2-C_6-alkyl which is substituted by -COOH, -SO_3H, -OSO_3H, -OPO_3H_2, or by a radical -NH-C(O)-O-G' wherein G' is the radical of lactobionic acid, hyaluronic acid or sialic acid, in particular C_2-C_4-alkyl which is substituted by -SO_3H or

$-OSO_3H$; a radical $-CONY_5Y_6$ wherein Y_5 is C_1-C_6-alkyl substituted by sulfo, in particular C_2-C_4-alkyl substituted by sulfo, and Y_6 is hydrogen, for example the radical $-C(O)-NH-C(CH_3)_2-CH_2-SO_3H$; or $-SO_3H$; or a suitable salt thereof. Particular preferred anionic substituents of B or B' are -COOH, $-SO_3H$, o-, m- or p-sulfophenyl, o-, m- or p-sulfomethylphenyl or a radical $-CONY_5Y_6$ wherein Y_5 is C_2-C_4-alkyl substituted by sulfo, and Y_6 is hydrogen, especially carboxy.

(iii) cationic substituents:

Preferred cationic substituents of B or B' are C_1-C_4-alkyl, in particular C_1-C_2-alkyl, which is in each case substituted by $-NR_9R_9'R_9''^+An^-$; or a radical $-C(O)OY_7$ wherein Y_7 is C_2-C_6-alkyl, in particular C_2-C_4-alkyl, which is in each case substituted by $-NR_9R_9'R_9''^+An^-$ and is further unsubstituted or substituted by hydroxy. R_9, R_9' and R_9'' are each independently of another preferably hydrogen or C_1-C_4-alkyl, more preferably methyl or ethyl and particularly preferably methyl. Examples of suitable anions An^- are Hal^-, wherein Hal is halogen, for example Br^-, F^-, J^- or particularly Cl^-, furthermore HCO_3^-, CO_3^{2-}, $H_2PO_3^-$, HPO_3^{2-}, PO_3^{3-}, HSO_4^-, SO_4^{2-} or the radical of an organic acid such as $OCOCH_3^-$ and the like. A particularly preferred cationic substituent of B or B' is a radical $-C(O)OY_7$ wherein Y_7 is C_2-C_4-alkyl, which is substituted by $-N(C_1\text{-}C_2\text{-alkyl})_3^+An^-$ and is further substituted by hydroxy, and An^- is an anion, for example the radical $-C(O)O-CH_2-CH(OH)-CH_2-N(CH_3)_3^+An^-$.

(iv) zwitterionic substituents $-R_3$-Zw:

R_3 is a preferably a carbonyl, ester or amide functional group and more preferably an ester group -C(O)-O-.

Suitable anionic groups of the moiety Zw are for example $-COO^-$, $-SO_3^-$, $-OSO_3^-$, $-OPO_3H^-$ or bivalent $-O-PO_2^-$- or $-O-PO_2^--O-$, preferably a group $-COO^-$ or $-SO_3^-$ or a bivalent group $-O-PO_2^-$-, and in particular a group $-SO_3^-$.

Suitable cationic groups of the moiety Zw are for example a group $-NR_9R_9'R_9''^+$ or a bivalent group $-NR_9R_9''^+$-, wherein R_9, R_9' and R_9'' are as defined above, and are each independently of the other, preferably hydrogen or C_1-C_6-alkyl, preferably hydrogen or C_1-C_4-alkyl and most preferably each methyl or ethyl.

The moiety Zw is for example C_2-C_{30}-alkyl, preferably C_2-C_{12}-alkyl, and more preferably C_3-C_8-alkyl, which is in each case uninterrupted or interrupted by -O- and substituted or interrupted by one of the above-mentioned anionic and cationic groups each, and, in

addition, is further unsubstituted or substituted by a radical $-OY_8$, wherein Y_8 is hydrogen or the acyl radical of a carboxylic acid.

Y_8 is preferably hydrogen or the acyl radical of a higher fatty acid.

Zw is preferably C_2-C_{12}-alkyl and even more preferably C_3-C_8-alkyl which is substituted or interrupted by one of the above-mentioned anionic and cationic groups each, and in addition may be further substituted by a radical $-OY_8$.

A preferred group of zwitter-ionic substituents $-R_3-Z$ corresponds to the formula

$$-C(O)O-(alk'')-N(R_9)_2^+-(alk')-An^- \quad \text{or}$$

$$-C(O)O-(alk'')-O-PO_2^--(O)_{0-1}-(alk''')-N(R_9)_3^+$$

wherein R_9 is hydrogen or C_1-C_6-alkyl; An^- is an anionic group $-COO^-$, $-SO_3^-$, $-OSO_3^-$ or $-OPO_3H^-$, preferably $-COO^-$ or $-SO_3^-$ and most preferably $-SO_3^-$, alk' is C_1-C_{12}-alkylene, (alk'') is C_2-C_{24}-alkylene which is unsubstituted or substituted by a radical $-OY_8$, Y_8 is hydrogen or the acyl radical of a carboxylic acid, and (alk''') is C_2-C_8-alkylene.

(alk') is preferably C_2-C_8-alkylene, more preferably C_2-C_6-alkylene and most preferably C_2-C_4-alkylene. (alk'') is preferably C_2-C_{12}-alkylene, more preferably C_2-C_6-alkylene and particularly preferably C_2-C_3-alkylene which is in each case unsubstituted or substituted by hydroxy or by a radical $-OY_8$. (alk''') is preferably C_2-C_4-alkylene and more preferably C_2-C_3-alkylene. R_9 is hydrogen or C_1-C_4-alkyl, more preferably methyl or ethyl and particularly preferably methyl. A preferred zwitterionic substituent of B or B' is of formula

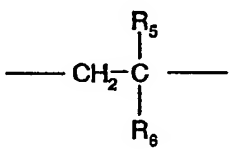
$$-C(O)O-CH_2-CH(OY_8)-CH_2-O-PO_2^--(CH_2)_2-N(CH_3)_3^+,$$

wherein Y_8 is hydrogen or the acyl radical of a higher fatty acid.

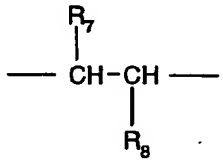
In one embodiment of the invention one of B and B' may also be the radical of a hydrophobic comonomer which includes especially those customarily used in the manufacture of contact lenses. Suitable hydrophobic vinylic comonomers include, without the list being exhaustive acrylonitrile, methacrylonitrile, vinyl-C_1-C_{18}-alkanoates, C_2-C_{18}-alkenes, C_2-C_{18}-haloalkenes, styrene, C_1-C_6-alkylstyrene, C_2-C_{10}-perfluoroalkyl acrylates and methacrylates or correspondingly partially fluorinated acrylates and methacrylates, C_3-C_{12}-perfluoroalkyl-ethyl-thiocarbonylaminoethyl acrylates and methacrylates, acryloxy- and methacryloxy-alkylsiloxanes, N-vinylcarbazole and the like. Examples of suitable

hydrophobic vinylic comonomers include acrylonitrile, methacrylonitrile, vinyl acetate, vinyl propionate, vinylbutyrate, vinyl valerate, styrene, chloroprene, vinyl chloride, vinylidene chloride, 1-butene, butadiene, vinyltoluene, perfluorohexylethylthiocarbonylaminoethyl methacrylate, trifluoroethyl methacrylate, hexafluoroisopropyl methacrylate, hexafluorobutyl methacrylate, tris-trimethylsilyloxy-silyl-propyl methacrylate, 3-methacryloxypropylpenta-methyldisiloxane and bis(methacryloxypropyl)tetramethyldisiloxane.

B denotes for example a radical of formula


(4a)

or

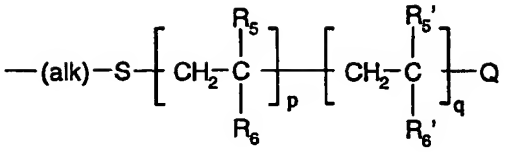

(4b),

wherein R_5 is hydrogen or C_1-C_4-alkyl, preferably hydrogen or methyl; R_6 is a hydrophilic substituent, wherein the above given meanings and preferences apply; R_7 is C_1-C_4-alkyl, phenyl or a radical -C(O)OY_9, wherein Y_9 is hydrogen or unsubstituted or hydroxy-substituted C_1-C_4-alkyl; and R_8 is a radical -C(O)Y_9' or -CH_2-C(O)OY_9' wherein Y_9' independently has the meaning of Y_9.

R_7 is preferably C_1-C_2-alkyl, phenyl or a group -C(O)OY_9. R_8 is preferably a group -C(O)OY_9' or -CH_2-C(O)OY_9' wherein Y_9 and Y_9' are each independently of the other hydrogen, C_1-C_2-alkyl or hydroxy-C_1-C_2-alkyl. Particularly preferred -CHR_7-CHR_8- units according to the invention are those wherein R_7 is methyl or a group -C(O)OY_9 and R_8 is a group -C(O)OY_9' or -CH_2-C(O)OY_9' wherein Y_9 and Y_9' are each hydrogen, C_1-C_2-alkyl or hydroxy-C_1-C_2-alkyl.

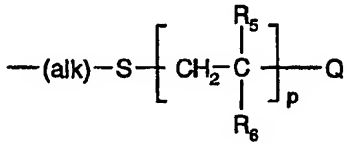
B' independently may have one of the meanings given above for B or is the radical of a hydrophobic comonomer, for example the radical of one of the above-given hydrophobic comonomers.

If (oligomer) is a telomer radical of formula (3a), the radical -(alk)-S-$[B]_p$-$[B']_q$-Q preferably denotes a radical of formula



(3a') and

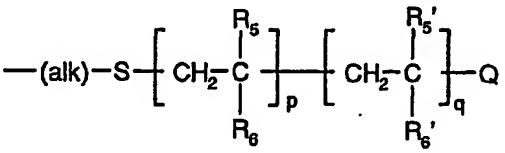
even more preferably of the formula



(3a''),

wherein for R_5, R_6, Q, p and q the above-given meanings and preferences apply, for R_5' independently the meanings and preferences given before for R_5 apply, and for R_6' Independently the meanings and preferences given before for R_6 apply or R_6' is a hydrophobic substituent selected from the group consisting of hydrogen, -CN, C_1-C_{18}-alkanoyl, C_1-C_{16}-alkyl, C_1-C_{16}-haloalkyl, phenyl, C_1-C_6-alkylphenyl, C_2-C_{10}-perfluoroalkyloxycarbonyl or a corresponding partially fluorinated alkyloxycarbonyl radical, C_3-C_{12}-perfluoroalkyl-ethyl-thiocarbonylaminoethyloxycarbonyl, alkylsiloxyloxycarbonyl and carbazolyl .

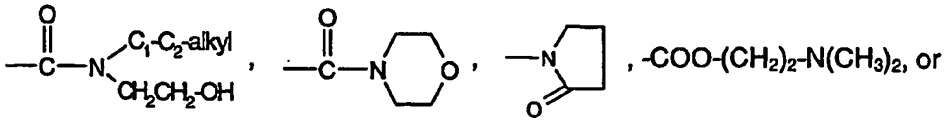
A preferred group of suitable hydrophilic macromers according to the invention comprises compounds of the above formula (1) wherein R is hydrogen or methyl, R_1 is hydrogen, methyl or carboxyl, R_1' is hydrogen, A is a radical of the above formula (2a), (2b) or (2e), wherein n and m are each 0 or 1, X and X_1 are each independently of the other -O- or -NH-, A_1 is unsubstituted or hydroxy-substituted -O-C_2-C_8-alkylene or a radical -O-C_2-C_6-alkylene-NH-C(O)-, A_2 is C_1-C_4-alkylene, phenylene or benzylene, (alk*) is C_2-C_4-alkylene, and (oligomer) denotes a radical of formula



(3a'),

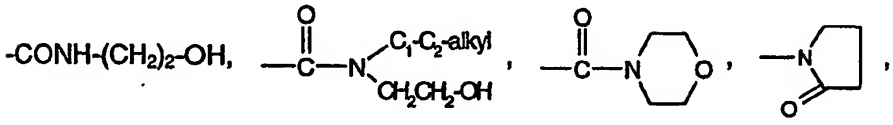
wherein (alk) is C_2-C_6-alkylene, Q is a monovalent group that is suitable to act as a polymerization chain-reaction terminator, p and q are each an integer of from 0 to 100 and the total of (p+q) is from 5 to 100, R_5 and R_5' are each independently of the other hydrogen or methyl, and for R_6 and R_6' each independently of the other the meanings and preferences given before apply. One particularly preferred embodiment of the above outlined hydrophilic macromers comprises those wherein q is 0, p is from 5 to 100, R_5 is

hydrogen or methyl, and R_6 is a radical $-CONH_2$, $-CON(CH_3)_2$, $-CONH-(CH_2)_2-OH$,



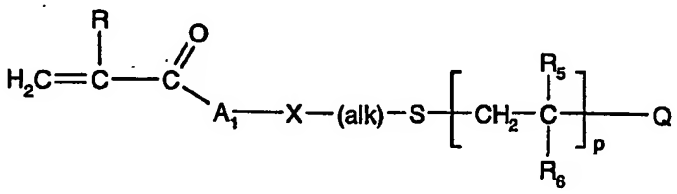
$-COO-(CH_2)_2-N(CH_3)_2$, or

$-COO(CH_2)_{2-4}-NHC(O)-O-G$ wherein -O-G is the radical of trehalose. A further preferred embodiment of the above outlined hydrophilic macromers comprises those wherein p is from 4 to 99, q is from 1 to 96 wherein in the total of (p+q) is from 5 to 100, R_5 and R_5' are each independently hydrogen or methyl, R_6 is a radical $-CONH_2$, $-CON(CH_3)_2$,



$-COO-(CH_2)_2-N(CH_3)_2$, or $-COO(CH_2)_{2-4}-NHC(O)-O-G$ wherein -O-G is the radical of trehalose, and R_6' independently has the meaning of R_6 or is carboxy, subject to the proviso that R_6 and R_6' are different.

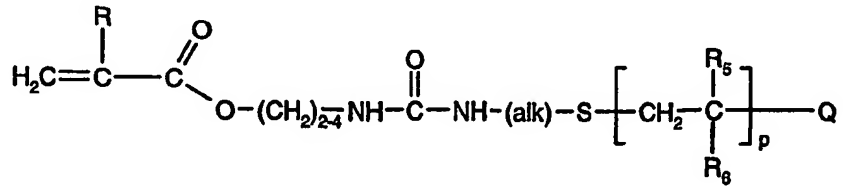
A more preferred group of suitable hydrophilic macromonomers according to the invention comprises compounds of formula



(1a),

wherein R is hydrogen or methyl, A_1 is $-O-(CH_2)_{2-4}-$, $-O-CH_2-CH(OH)-CH_2-$ or a radical $-O-(CH_2)_{2-4}-NH-C(O)-$, X is -O- or -NH-, (alk) is C_2-C_4-alkylene, Q is a monovalent group that is suitable to act as a polymerization chain-reaction terminator, p is an integer from 5 to 50, R_5 is hydrogen or methyl, and for R_6 the above given meanings and preferences apply.

A particularly preferred embodiment of the invention relates to hydrophilic macromonomers of the formula



(1b),

wherein for R, R_5, R_6, Q, (alk) and p the above-given meanings and preferences apply. A particularly preferred group of hydrophilic macromonomers are compounds of the above formula (1b) wherein R is hydrogen or methyl, (alk) is C_2-C_4-alkylene, R_5 is hydrogen or methyl, p is an integer of 5 to 50, Q is as defined before, and for R_6 the above given meanings and preferences apply.

If (oligomer) is a radical (ii) of formula (3b), Q' in formula (3b) is for example C_1-C_{12}-alkyl, phenyl or benzyl, preferably C_1-C_2-alkyl or benzyl and in particular methyl. R_{29} is preferably unsubstituted or hydroxy-substituted C_1-C_4-alkyl and in particular methyl. u is preferably an integer from 2 to 150, more preferably from 5 to 100, even more preferably from 5 to 75 and particularly preferably from 10 to 50.

If (oligomer) is a radical of formula (3b'), the above given meanings and preferences apply for the variables X, R_{29} and u contained therein.

If (oligomer) denotes a radical (iv) of formula (3c),R_2 and R_2' are each preferably ethyl or in particular methyl; v is preferably an integer from 2 to 150, more preferably from 5 to 100, even more preferably from 5 to 75 and particularly preferably from 10 to 50; Q" is for example hydrogen; and An^- is as defined before.

If (oligomer) denotes an oligopeptide radical (v) of formula (3d) or 3d'), R_4 is for example hydrogen, methyl, hydroxymethyl, carboxymethyl, 1-hydroxyethyl, 2-carboxyethyl, isopropyl, n-, sec. or iso-butyl, 4-amino-n-butyl, benzyl, p-hydroxybenzyl, imidazolylmethyl, indolylmethyl or a radical $-(CH_2)_3-NH-C(=NH)-NH_2$. t is preferably an integer from 2 to 150, more preferably from 5 to 100, even more preferably from 5 to 75 and particularly preferably from 10 to 50.

If (oligomer) denotes a polyoxyalkylene radical (vi) of formula (3e), R_{30} is preferably hydrogen or C_1-C_{18}-alkyl, more preferably hydrogen or C_1-C_{12}-alkyl, even more preferably hydrogen, methyl or ethyl, and particularly preferably hydrogen or methyl. ($alk^{"}$) is preferably a C_2-C_3-alkylene radical. z is preferably 0. r and s are each independently preferably an integer from 0 to 100 wherein the total of (r+s) is 5 to 100. r and s are each independently more preferably an integer from 0 to 50 wherein the total of (r+s) is 8 to 50.

In a particularly preferred embodiment of the polyoxyalkylene radicals (oligomer), r is an integer from 8 to 50 and particularly 9 to 25, and s is 0.

(oligomer) as the radical of an oligosaccharide (vii) may be, for example, a di- or polysaccharide including carbohydrate containing fragments from a biopolymer. Examples are the radical of a cyclodextrin, trehalose, cellobiose, maltotriose, maltohexaose, chitohexaose or a starch, hyaluronic acid, deacetylated hyaluronic acid, chitosan, agarose, chitin 50, amylose, glucan, heparin, xylan, pectin, galactan, glycosaminoglycan, mucin, dextran, aminated dextran, cellulose, hydroxyalkylcellulose or carboxyalkylcellulose oligomer, each of which with a molecular weight average weight of, for example, up to 25000, preferably up to 10000. Preferably the oligosaccharide according to (vii) is the radical of a cyclodextrin with a maximum of 8 sugar units.

In the above formulae (2a), (2b), (2c), (2d) and (2e), the left bond is in each case attached to the double bond whereas the right bond is linked to the oligomer. Formulae (3a), (3a') and (3e) are to be understood as a statistic description of the respective oligomeric radicals, that is to say, the orientation of the monomers and the sequence of the monomers (in case of copolymers) are not fixed in any way by said formulae. The arrangement of B and B' in formula (3a) or of the ethyleneoxide and propyleneoxide units in formula (3e) thus may be random or blockwise. Throughout the whole description, anions such as -COOH or $-SO_3H$ groups always include suitable salt forms, preferably biomedical or especially ophthalmically acceptable salts, in particular $-COO^-Ka^+$ and $-SO_3^-Ka^+$ groups wherein Ka^+ is a cation such as an alkali metal cation or an ammonium cation.

The weight average molecular weight of the macromonomers of the invention depends principally on the desired properties and is for example from 300 to 50000, preferably from 300 to 12000, more preferably from 300 to 8000, even more preferably 300 to 5000, and particularly preferably from 500 to 2000.

The macromonomers of formula (1) may be prepared by methods, for example as described in WO 99/57581.

The hydrophilic monomers and macromonomers may be applied to the initiator-modified bulk material surface and polymerized there according to processes known per se. For

example, the bulk material is immersed in a solution of the monomer or macromonomer, or a layer of monomer or macromonomer is first of all deposited on the modified bulk material surface, for example, by dipping, spraying, spreading, knife coating, pouring, rolling, spin coating or vacuum vapor deposition. The polymerization of the macromonomer on the bulk material surface then may be initiated , for example, thermally by the action of heat or preferably by irradiation, particularly by UV radiation. Suitable light sources for the irradiation are known to the artisan and comprise for example mercury lamps, high pressure mercury lamps, xenon lamps, carbon arc lamps or sunlight. The time period of irradiation may depend for example on the desired properties of the resulting composite material but is usually in the range of up to 30 minutes, preferably from 10 secondes to 10 minutes, and particularly preferably from 0.5 to 5 minutes. The irradiation may be carried out under ambient conditions or in an atmosphere of an inert gas, for example nitrogen. After the polymerization, any non-covalently bonded polymers, oligomers or non-reacted monomer or macromonomers formed can be removed, for example by treatment with suitable solvents.

By means of the above-described coating process, hydrophilic monomers may be grafted to the bulk material surface with formation of a coating having for example a so-called brush-type structure.

Most important, the grafting of the macromonomers to the bulk material surface yields a coating having for example a so-called bottle brush-type structure (BBT) composed of tethered "hairy" chains. Such BBT structures in one embodiment comprise a long hydrophilic or hydrophobic backbone which carries relatively densely packed comparatively short hydrophilic side chains (called primary bottle brushes). Another embodiment relates to secondary bottle brushes which are characterized in that the hydrophilic side chains themselves carry densely packed hydrophilic "secondary" side chains. Polymeric coatings of said primary and secondary BBT structures to a certain extent mimic highly water-retaining structures occurring in the human body, for example in cartilage or mucosal tissue.

The coating thickness of the hydrophilic surface coating (b) depends principally on the desired properties. In case of macromonomers it can be used, for example, from 0.001 to 1000 µm, preferably from 0.01 to 500 µm, more preferably from 0.01 to 100 µm, even more

preferably from 0.05 to 50 µm, especially preferably from 0.1 to 5 µm and particularly preferably from 0.1 to 1 µm. A particularly suitable range is from 0.2 to 0.6 µm.

The complete coating of the bulk material according to the invention consists (a) of a polyionic material comprising one polyelectrolyte or preferably one or more bilayers of polyelectrolytes and (b) of an upper hydrophilic coating obtainable by grafting one or more hydrophilic monomers or preferably macromonomers onto the surface, wherein the latter makes up at least 50 %, preferably from 75 to 98 % and particularly preferably from 80 to 95 % of the total thickness of the fully hydrated coating.

A further embodiment of the invention is a biomedical device, e.g. an ophthalmic device, preferably a contact lens including both hard and particularly soft contact lenses, an intraocular lens or artificial cornea, comprising a composite material according to the invention and particular a composite material comprising a macromonomer-based surface coating. The inventive materials are further useful for example as wound healing dressings, eye bandages, materials for the sustained release of an active compound such as a drug delivery patch, moldings that can be used in surgery, such as heart valves, vascular grafts, catheters, artificial organs, encapsulated biologic implants, e.g. pancreatic islets, materials for prostheses such as bone substitutes, or moldings for diagnostics, membranes or biomedical instruments or apparatus.

The biomedical devices, e.g. ophthalmic devices according to the invention have a variety of unexpected advantages over those of the prior art which make those devices very suitable for practical purposes,e.g. as contact lens for extended wear or intraocular lens. For example, they do have a high surface wettability which can be demonstrated by their contact angles, their water retention ability and their water-film break up time or tear film break up time (TBUT).

The TBUT plays an particularly important role in the field of ophthalmic devices such as contact lenses. Thus the facile movement of an eyelid over a contact lens has proven important for the comfort of the wearer; this sliding motion is facilitated by the presence of a continuous layer of tear fluid on the contact lens, a layer which lubricates the tissue/lens interface. However, clinical tests have shown that currently available contact lenses partially dry out between blinks, thus increasing friction between eyelid and the lens. The increased

friction results in soreness of the eyes and reduced movement of the contact lenses. Taking into account the average time period between two blinks of an eye it follows that a wettable and biocompatible contact lens should hold a continuous layer of tear fluid for more than 10 seconds and preferably for more than 15 seconds. Whereas current biomedical materials in general have TBUTs of well below 10 seconds and thus do not reach this target, the composite materials of the present invention have TBUTs of >10 seconds and especially > 15 seconds. In addition, the TBUT of commercial contact lenses may be improved considerably by applying a surface coating according to the invention. For example, the TBUT of commercial contact lenses such as Focus Dailies™, Focus New Vues® or Lotrafilcon A lenses, may be increased by more than 50 % or, according to a particularly preferred embodiment, by ≥100 % by applying a surface coating according to the invention. On the base curve of a contact lens, the pronounced lubricity of the coating facilitates the on-eye lens movement which is essential for extended wear of contact lenses. Moreover, the composite materials of the invention provide additional effects being essential for lenses for extended wear, such as an increased thickness of the pre-lens tear film and of the topical lipid layer of the tear film which each contributes substantially to low microbial adhesion and resistance to deposit formation. Due to the extremely soft and lubricious character of the novel surface coatings, biomedical articles such as in particular contact lenses made from an inventive composite material show a superior wearing comfort including improvements with respect to late day dryness, long term (overnight) wear and acute vision on awake. The novel surface coatings moreover interact in a reversible manner with occular mucus which contributes to the improved wearing comfort.

In addition, biomedical devices, e.g. ophthalmic devices such as contact lenses, comprising a composite material of the invention have a very pronounced biocompatibility combined with good mechanical properties. For example, the devices are blood compatible and have a good tissue integration. In addition, there are generally no adverse eye effects observed, while the adsorption of proteins or lipids is low, also the salt deposit formation is lower than with conventional contact lenses. Generally, there is low fouling, low microbial adhesion and low bioerosion while good mechanical properties can be for example found in a low friction coefficient and low abrasion properties. Moreover, the dimensional stability of the composite materials of the invention is excellent. In addition, the attachment of a hydrophilic surface coating at a given bulk material according to the invention does not affect its visual transparency.

In summary, the ophthalmic devices according to the invention, such as intraocular lenses and artificial cornea or particularly contact lenses, provide a combination of low spoilation with respect to cell debris, cosmetics, tear components, lipids, proteins, salts, dust or dirt, solvent vapors or chemicals, with a high comfort for the patient wearing such opthalmic devices in view of the soft hydrogel surface which for example provides a very good on-eye movement of the ohthalmic device.

Biomedical devices such as renal dialysis membranes, blood storage bags, pacemaker leads or vascular grafts made of the composite materials of the invention resist fouling by proteins by virtue of the continuous layer of bound water, thus reducing the rate and extent of thrombosis. Blood-contacting devices fabricated according to the present invention are therefore haemocompatible and biocompatible.

In the examples, if not indicated otherwise, amounts are amounts by weight, temperatures are given in degrees Celsius. Tear break-up time values in general relate to the pre-lens tear film non-invasive break-up time (PLTF-NIBUT) that is determined following the procedure published by M. Guillon et al., Ophthal. Physiol. Opt. 9, 355-359 (1989) or M. Guillon et al., Optometry and Vision Science 74, 273-279 (1997). Average advancing and receding water contact angles of coated and non-coated lenses are determined with the dynamic Wilhelmy method using a Krüss K-12 Instrument (Krüss GmbH, Hamburg, Germany). Wetting force on the solid is measured as the solid is immersed in or withdrawn from a liquid of known surface tension.

Example A-1 (Preparation of aminofunctionalized contact lenses by attaching a bilayer)

a.) A 0.001M polyacrylic acid (PAA) solution ($M_n \approx$ 68000) is prepared by adding 0.29 grams of a 25% aqueous PAA stock solution to 1000ml of ultra-pure water in a beaker. Then the pH of the solution is adjusted to 2.5 by adding 1N HCl and the solution is filtered using qualitative filter paper.

b.) A 0.001M polyallylamine hydrochloride (PAH) solution ($M_n \approx$ 70000) is prepared by adding 0.09 g PAH (solid) into a small beaker; dissolving in ultra-pure (UP) water and transfering into a bigger beaker with a final volume of 1000 ml aqueous solution. The pH is then adjusted to 4.5 as measured with a pH meter. The solution is then filtered using qualitative filter paper.

c.) Swollen non-coated Lotrafilcon A lenses (polysiloxane/perfluoroalkylpolyether co-polymer) in iso-propanol (IPA) are individually immersed into the solution a.) for 5 minutes. After this time, the lenses are withdrawn from the solution a.) and directly immersed into the solution b.) for additional 5 minutes. No water rinse is done between these two dips. After this, the lenses are released into UP water and stored at 4°C for further use.

Example A-2 (Preparation of aminofunctionalized contact lenses by attachment of a bilayer)

a.) A 0.1 % by weight solution of a branched polyacrylic acid (Carbopol® 981 NF) is prepared by adding 0.05 g of Carbopol® 981 NF (BFGoodrich) to 50 ml of isopropanol-ultra-pure water mixture (1:4) in a beaker. After complete dissolution (overnight), the pH of the solution is adjusted to 2.5 by adding 1N HC1 and the solution is filtered using qualitative filter paper.

b.) 100 ml of 0.05 % solution of polyethyleneimine (PEI) is prepared by adding 0.1 g of 50 % aqueous PEI stock solution into a mixture of isopropanol-ultra-pure water 1:4. The pH is then adjusted to 3.5 by adding 1N HCl as measured by pH meter. The solution is then filtered using qualitative filter paper.

c.) Swollen non-coated Lotrafilcon A lenses in iso-propanol (IPA) are individually immersed into the solution a.) for 10 minutes. The lenses are withdrawn from the solution a.) rinsed with ultra-pure water and immersed into the solution b.) for additional 10 minutes. After this, the lenses are released into ultra-pure water and stored at 4°C for further use.

Example B-1 (Surface binding of reactive photoinitiator molecules)

The aminofunctionalized contact lenses from Example A-1 are first immersed into acetonitrile for 1 hour (20 ml acetonitrile / lens). The lenses are then withdrawn and directly immersed into a 1% by weight solution of the reactive photoinitiator prepared by the addition reaction from isophorone diisocyanate and 4-(2-hydroxyethoxy)phenyl 2-hydroxy-2-propyl ketone (Darocure 2959) (synthesis see EP 0 632 329) in acetonitrile. 3 drops of triethylamine (TEA) are then added to the solution. The amino groups on the lens surface react with the isocyanato groups of the photoinitiator molecules for 12 hours. After this time, the lenses are withdrawn from the reaction solution, 3x washed and extracted in acetonitrile for 8 hours and dried under reduced pressure for 2 hours. The dried lenses are subsequently used for photografting.

Example B-2 (Surface binding of the reactive photoinitiator molecules)

The aminofunctionalized contact lenses from Example A-2 are dried to the constant mass under reduced pressure. The lenses are then directly immersed into 1% by weight acetonitrile solution of the reactive photoinitiator prepared by the addition reaction from isophorone diisocyanate and 2-dimethylamino-2-benzyl-1-[4-(2-hydroxyethoxy)phenyl]-butan-1-one (synthesis see WO 96/20796(20 ml solution/lens). 3 drops of triethylamine (TEA) are then added to the solution. The amino groups on the lens surface react with the isocyanato groups of the photoinitiator molecules for 12 hours. After this time, the lenses are withdrawn from the reaction solution, 3x washed and extracted in acetonitrile for 6 hours and dried under reduced pressure for 2 hours. The dried lenses are subsequently used for photografting.

Example C-1 (Acrylamide telomer (M_n 2000) synthesis

A 1000 mL round bottom flask is charged with a solution of 71.1g (1 mol) Acrylamide, 4.93g (18.2 mmol) α,α'-azodiisobutyramidine dihydrochloride and 4.93 g (36.4 mmol) cysteamin-hydrochloride in 400 ml of water. The clear and slightly yellowish solution is acidified with a few drops of hydrochloric acid to pH3. The stirred acidic solution is evacuated to 50 mbar and filled with argon. This is repeated three times. With a constant stream of Argon, this solution is poured into a 500 ml dropping funnel which is put onto an 'flow-through-reactor' consisting of an 1000ml three-necked round-bottom flask, reflux condenser, thermometer, magnetic stirrer and a 30 cm Liebig-condenser, which is filled with glass wool. The whole apparatus is constantly purged with argon. The dropping funnel is put onto the Liebig condenser, which is heated to 65°C. The flask is heated to 60°C. The solution is slowly dropped through the Liebig–condenser into the stirred flask. This takes 2.5 hrs. During this time the temperature in the flask is kept between 58-65°C. After the completed addition, the solution is stirred for 2hrs at 60°C.
NaOH is added to the clear and slightly yellowish solution until pH 10 is reached. The product is purified through reverse osmosis, using Millipore cartridge with a cut-off at 1000 Da and freeze-dried. A bright-white solid product is obtained (NH_2 0.34mEq/g ,sulfur-value of the elemental analysis (0.33mEq/g); M_n 2000g/Mol).

Example C-2 (Acrylamide telomer (M_n 1350) synthesis

A 1000 mL round bottom flask is charged with a solution of 99.5 g (1.46 mol) acrylamide, 1.27 g (4.68 mmol) α,α'-azodiisobutyramidine dihydrochloride and 15.9 g (0.14 mol) cysteaminhydrochloride in 300 ml of water. The clear and slightly yellowish solution is acidified with a few drops of hydrochloric acid (32%) to pH 3. The stirred acidic solution is evacuated to 50 mbar and filled with argon. This is repeated three times. With a constant stream of argon, this solution is poured into a 500 ml dropping funnel which is put onto an 'flow-through-reactor' consisting of an 1000ml three-necked round-bottom flask, reflux condenser, thermometer, magnetic stirrer and a 30 cm Liebig-condenser, which is filled with glass wool. The whole apparatus is constantly purged with argon. The dropping funnel is put onto the Liebig condenser, which is heated to 65°C. The flask is heated to 60°C. The solution is slowly dropped through the Liebig–condenser into the stirred flask. This takes 2 hrs. During this time the temperature in the flask is kept between 58-65°C. After the completed addition, the solution is stirred for 2 hrs at 60°C.
NaOH is added to the clear and slightly yellowish solution until pH 10 is reached. The product is purified through reverse osmosis, using Millipore cartridge with a cut-off at 1000 Da and then freeze-dried for 18 hrs.. A bright-white solid product is obtained (NH_2 0.70mEq/g, sulfur-value of the elemental analysis (0.73mEq/g; M_n 1350g/Mol).

Example C-3 (N,N-dimethyl acrylamide telomer (M_n 1850) synthesis

A 2000 mL round bottom flask is charged with a solution of 198.2 g (2 mol) N,N-dimethyl acrylamide, 2.72 g (10 mmol) α,α'-azodiisobutyramidine dihydrochloride and 24.8 g (0.22 mol) cysteaminhydrochloride in 600 ml of water. The clear and slightly yellowish solution is acidified with a few drops of Hydrochloric Acid (32%) to pH3. The stirred acidic solution is evacuated to 50 mbar and filled with argon. This is repeated three times.With a constant stream of argon, this solution is poured into a 1000 ml dropping funnel which is put onto an 'flow-through-reactor' consisting of an 1000ml three-necked round-bottom flask, reflux condenser, thermometer, magnetic stirrer and a 30 cm Liebig-condenser, which is filled with glass wool. The whole apparatus is constantly purged with argon.
The dropping funnel is put onto the Liebig condenser, which is heated to 60°C. The flask is also heated to 60°C. The solution is slowly dropped through the Liebig–condenser into the stirred flask. This takes 2.5 hrs. During this time the temperature in the flask is kept between 58-65°C. After the completed addition, the solution is stirred for 2hrs at 60°C.30 % NaOH solution is added to the clear and slightly yellowish solution until pH 10 is reached. The

product is purified through reverse osmosis, using Millipore cartridge with a cut-off at 1000 Da and freeze-dried. A bright-white solid product is obtained (NH_2 0.54mEq/g; M_n ~1850 g/Mol).

Example D-1 (Preparation of IEM-functionalized acrylamide telomer solution)

7.5 g of acrylamide telomer with amino end group (amine titration = 0.70 mEq/g), prepared by Example C-2 are dissolved in 80 ml of HPLC water. Argon is then let to bubble through the solution for the period of about 30 minutes. This mixture is then added to the equimolar amount (0.81 g) of isocyanatoethyl methacrylate (IEM, isocyanate titration = 6.45 mEq/g) under stirring. The whole mixture is then stirred under argon flow for 12 hours. After adding of 0.8 g of NaCl to the solution and 10 minutes stirring, the mixture is filtered through 0.45 µm Teflon filter, degassed by repeated (3x) evacuation and bubbling with argon in order to remove oxygen and used for photografting.

Example D-2 (Preparation of IEM-functionalized N,N-dimethylacrylamide telomer solution)

5 g of N,N-dimethylacrylamide telomer with amino end group (amine titration = 0.53 mEq/g), prepared by Example C-3 are dissolved in 100 ml of HPLC water. Argon is then let to bubble through the solution for the period of about 30 minutes. This mixture is then added to the equimolar amount (0.41 g) of isocyanatoethyl methacrylate (IEM, isocyanate titration = 6.45 mEq/g) under stirring. The whole mixture is then stirred under argon flow for 12 hours. After adding of 1.0 g of NaCl to the solution and 10 minutes stirring, the mixture is filtered through 0.45 µm Teflon filter, degassed with nitrogen in order to remove oxygen and used for photografting.

Example E-1 (Photografting of IEM-functionalized acrylamide telomers onto a contact lens surface

1 ml of the IEM-functionalized acrylamide telomer solution from Example D-1 is introduced into a small Petri dish of a volume of about 2 ml in a glove box. The dried lens from Example B-1, carrying covalently linked photoinitiator molecules on its surface, is then placed into this solution and an additional 0.5 ml of the degassed solution is added on the lens in order to cover the whole lens with the solution. After 10 minutes, the Petri dish with the lens in the solution is exposed to 14.5 mW/cm^2 ultraviolet light for a period of about 1.5 minutes.

The modified lens is then withdrawn from the solution, washed twice in destilled water, continuously extracted in ultra pure water for 16 h and analyzed by AFM, ATR-FTIR and contact angle measurements.
The thickness of the coating is in the range of 250-300 nm as determined by AFM.
Water/air contact angles on the modified lens are 0° adv., 0° rec., 0° hysteresis. In comparison, the contact angles of non-modified lens are 101° adv., 64° rec., 37° hysteresis.
The lens held continuous water layer on the surface for over 1 minute.

Example E-2 (Photografting of IEM-functionalized acrylamide telomers onto a contact lens surface)

Two lenses from Example B-1 are coated in accordance with Example E-1, but instead of 1.5 minutes of exposition, 1.7 minutes exposition time is used for photografting.
Water/air contact angles on the modified lenses are 0° adv., 0° rec., 0° hysteresis.

Example E-3 Photografting of IEM-functionalized N,N-dimethylacrylamide telomers onto a contact lens surface

1 ml of the IEM-functionalized N,N-dimethylacrylamide telomer solution from Example D-2 is introduced into a small Petri dish of a volume of about 2 ml in a glove box. The dried lens from Example B-1, carrying covalently linked photoinitiator molecules on its surface, is then placed into this solution and an additional 0.5 ml of the degassed solution is added on the lens in order to cover the whole lens with the solution. After 10 minutes, the Petri dish with the lens in the solution is exposed to 14.5 mW/cm^2 ultraviolet light for a period of about 1.5 minutes. The lens is then turned over and the exposition is repeated by applying 14.5 mW/cm^2 UV light for an additional 1.5 minutes.
The modified lens is then withdrawn from the solution, washed twice in destilled water, continuously extracted in ultra pure water for 16 h and analyzed by AFM, ATR-FTIR and contact angle measurements.
The thickness of the coating is in the range of 300-400 nm as determined by AFM.
Water/air contact angles on the modified lens are 0° adv., 0° rec., 0° hysteresis. In comparison, the contact angles of a non-modified lens are 101° adv., 64° rec., 37° hysteresis.

Example E-4 (Photografting of IEM-functionalized acrylamide telomers onto the contact lens surface under ambient conditions)

In a laminar flow hood, 1 ml of the IEM-functionalized acrylamide telomer solution from Example D-1 is introduced into a small Petri dish of a volume of about 2 ml. The dried lens from Example B-1, carrying covalently linked photoinitiator molecules on its surface, is then placed into this solution and an additional 0.5 ml of the degassed solution is added on the lens in order to cover the whole lens with the solution. After 10 minutes, the Petri dish with the lens in the solution is exposed to 2.05 mW/cm^2 ultraviolet light (MACAM-UV-Lamp) for a period of 2.5 minutes. The modified lens is then withdrawn from the solution, washed twice in destilled water, continuously extracted in ultra pure water for 16 h and analyzed by Atomic Force Microscopy (AFM), Fourier Transform Infrared-Attenuated Total Reflection Mode (ATR-FTIR) and contact angle measurements.

The thickness of the coating is in the range of 500-600 nm as determined by AFM.

Water/air contact angles on the modified lens are 0° adv., 0° rec., 0° hysteresis. In comparison, the contact angles of non-modified lens are 101° adv., 64° rec., 37° hysteresis. The lens held continuous water layer on the surface for over 1 minute.

Example E-5 (Photografting of IEM-functionalized N,N-dimethylacrylamide telomers onto the contact lens surface under ambient conditions)

In a laminar flow hood, 1 ml of the IEM-functionalized N,N-dimethylacrylamide telomer solution from Example D-2 is introduced into a small Petri dish of a volume of about 2 ml. The dried lens from Example B-1, carrying covalently linked photoinitiator molecules on its surface, is then placed into this solution and an additional 0.5 ml of the degassed solution is added on the lens in order to cover the whole lens with the solution. After 10 minutes, the Petri dish with the lens in the solution is exposed to 2.36 mW/cm^2 ultraviolet light (MACAM-UV-Lamp) for a period of 2.5 minutes. The modified lens is then withdrawn from the solution, washed twice in destilled water, continuously extracted in ultra pure water for 16 h and analyzed by AFM, ATR-FTIR and contact angle measurements.

Water/air contact angles on the modified lens are 6° adv., 0° rec., 6° hysteresis. In comparison, the contact angles of non-modified lens are 101° adv., 64° rec., 37° hysteresis.

Example E-6 Photografting of IEM-functionalized acrylamide telomers onto the contact lens surface

1 ml of the IEM-functionalized acrylamide telomer solution from Example D-1 is introduced into a small Petri dish of a volume of about 2.5 ml in a glove box. The dried lens from Example B-2, carrying covalently linked photoinitiator molecules on its surface, is then placed into this solution and an additional 1 ml of the degassed solution is added on the lens in order to cover the whole lens with the solution. After 10 minutes, the Petri dish with the lens in the solution is exposed to 14.5 mW/cm^2 ultraviolet light for a period of about 3 minutes.

The modified lens is then withdrawn from the solution, washed twice in destilled water, continuously extracted in ultra pure water for 16 h and analyzed by ATR-FTIR and contact angle measurements.

Water/air contact angles on the modified lens are 24° adv., 16° rec., 8° hysteresis. In comparison, the contact angles of non-modified lens are 101° adv., 64° rec., 37° hysteresis.

Claims:

1. A composite material comprising
(a) an inorganic or organic bulk material having attached to its surface a polyionic material that comprises covalently bound initiator moieties for radical polymerization; and
(b) a hydrophilic surface coating obtainable by applying one or more different ethylenically unsaturated hydrophilic monomers or macromonomers to the bulk material surface provided with the initiator radicals and polymerizing said monomers or macromonomers.

2. A composite material according to claim 1, which is a biomedical device, preferably an ophthalmic device such as a contact lens, intraocular lens or artificial cornea.

3. A composite material according to claim 1 or 2, wherein the bulk material comprises an organic polymer selected from a polyacrylate, polymethacrylate, polyacrylamide, poly(N,N-dimethylacrylamide), polymethacrylamide, polyvinyl acetate, polysiloxane, perfluoroalkyl polyether, fluorinated polyacrylate and -methacrylate and an amphiphilic segmented copolymer comprising at least one hydrophobic segment and at least one hydrophilic segment.

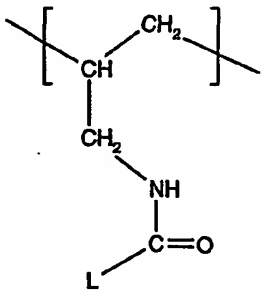
4. A composite material according to any one of claims 1 to 3, wherein the polyionic material consists of one ionic polymer.

5. A composite material according to any one of claims 1 to 3, wherein the polyionic material includes at least one bilayer, the bilayer comprising a first ionic polymer and a second ionic polymer having charges opposite of the charges of the first ionic polymer.

6. A composite material according to claim 5, wherein the bilayer(s) comprise(s) an anionic polymer selected from a linear polyacrylic acid, a branched polyacrylic acid, a polymethacrylic acid, a polyacrylic acid or polymethacrylic acid copolymer, a maleic or fumaric acid copolymer, a poly(styrenesulfonic acid), a polyamido acid, a poly(2-acrylamido-2-methylpropanesulfonic acid), and an alkylene polyphosphate, alkylene polyphosphonate, carbohydrate polyphosphate or carbohydrate polyphosphonate; and a cationic polymer selected from a polyallylamine (PAH); a polyethyleneimine (PEI); a polyvinylamine homo- or copolymer; a poly(vinylbenzyl-tri-C_1-C_4-alkylammonium salt); a polymer of an aliphatic or

araliphatic dihalide and an aliphatic N,N,N',N'-tetra-C_1-C_4-alkyl-alkylenediamine; a poly(vinylpyridin) or poly(vinylpyridinium salt); a poly (N,N-diallyl-N,N-di-C_1-C_4-alkyl-ammoniumhalide); a homo- or copolymer of a quaternized di-C_1-C_4-alkyl-aminoethyl acrylate or methacrylate; POLYQUAD®; and a polyaminoamide.

7. A composite material according to claim 5 or 6, wherein the bilayer(s) comprise(s) an anionic polymer selected from a linear or branched polyacrylic acid and an acrylic acid copolymer; and a cationic polymer selected from a polyallylamine homopolymer; a polyallylamine comprising modifier units of the formula



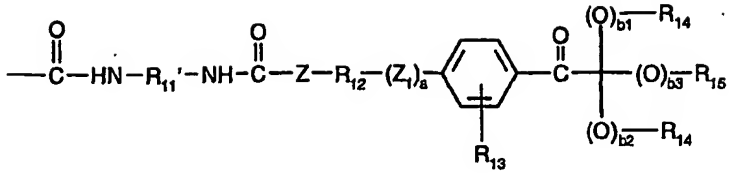
(5),

wherein L is C_2-C_6-alkyl which is substituted by two or more same or different substituents selected from the group consisting of hydroxy, C_2-C_5-alkanoyloxy and C_2-C_5-alkylamino-carbonyloxy; a polyvinylamine homo- or -copolymer; and a polyethyleneimine homopolymer.

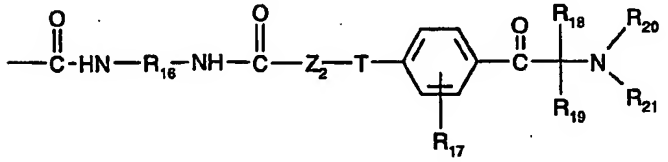
8. A composite material according to any one of claims 5 to 7, wherein the bilayer(s) comprise(s) a first anionic polymer and a second cationic polymer.

9. A composite material according to any one of claims 5 to 8, wherein the bilayer(s) are formed on the bulk material surface by a dip method involving the steps of
(i) applying a coating of a first ionic polymer to the bulk material by immersing the bulk material in a solution of the first ionic polymer; and
(ii) applying a coating of a second ionic polymer having charges opposite of the charges of the first ionic polymer to the bulk material by immersing the bulk material in a solution of the second ionic polymer.

10. A composite material according to any one of claims 5 to 9, wherein the bulk material comprises one or more bilayers having $-NH_2$ and/or -NH- groups attached to its surface, some of whose H atoms have been substituted by radicals of the formulae

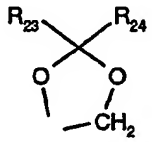


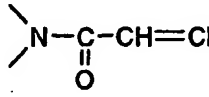
(12a) or



(12b),

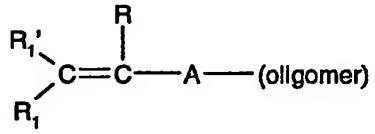
wherein Z is bivalent -O-, -NH- or -NR_{22}-; Z_1 is -O-, -O-(O)C-, -C(O)-O- or -O-C(O)-O-; R_{13} is H, C_1-C_{12}-alkyl, C_1-C_{12}-alkoxy or N-C_1-C_{12}-alkylamino; R_{14} and R_{15} are each independently of the other H, linear or branched C_1-C_8-alkyl, C_1-C_8-hydroxyalkyl or C_6-C_{10}-aryl, or the groups R_{14}-$(O)_{b1}$- and R_{14}-$(O)_{b2}$- together are -$(CH_2)_c$- wherein c is an integer from 3 to 5, or the groups R_{14}-$(O)_{b1}$-, R_{14}-$(O)_{b2}$- and R_{15}-$(O_1)_{b3}$- together are a radical of the formula



; R_{12} is a direct bond or linear or branched C_1-C_8-alkylene that is unsubstituted or substituted by -OH and/or is uninterrupted or interrupted by one or more groups -O-, -O-C(O)- or -O-C(O)-O-; R_{11}' is branched C_3-C_{18}-alkylene, unsubstituted or C_1-C_4-alkyl- or C_1-C_4-alkoxy-substituted C_6-C_{10}-arylene, or unsubstituted or C_1-C_4-alkyl- or C_1-C_4-alkoxy-substituted C_7-C_{18}-aralkylene, unsubstituted or C_1-C_4-alkyl- or C_1-C_4-alkoxy-substituted C_3-C_8-cycloalkylene, unsubstituted or C_1-C_4-alkyl- or C_1-C_4-alkoxy-substituted C_3-C_8-cycloalkylene-C_yH_{2y}- or unsubstituted or C_1-C_4-alkyl- or C_1-C_4-alkoxy-substituted -C_yH_{2y}-(C_3-C_8-cycloalkylene)-C_yH_{2y}- wherein y is an integer from 1 to 6; R_{16} independently has the same definitions as R_{11}' or is linear C_3-C_{18}-alkylene; R_{22} is linear or branched C_1-C_6-alkyl; T is bivalent -O-, -NH-, -S-, C_1-C_8-alkylene or  ; Z_2 is a direct bond or -O-$(CH_2)_d$- wherein d is an integer from 1 to 6 and the terminal CH_2 group of which is linked to the adjacent T in formula (10c); R_{17} is H, C_1-C_{12}-alkyl, C_1-C_{12}-alkoxy, N-C_1-C_{12}-alkylamino or -$NR_{25}R_{26}$ wherein R_{25} is C_1-C_8-alkyl and R_{26} is H or C_1-C_8-alkyl; R_{18} is linear or branched C_1-C_8-alkyl, C_2-C_8-alkenyl or C_6-C_{10}-aryl-C_1-C_8-alkyl; R_{19} independently of R_{18} has the same definitions as R_{18} or is C_6-C_{10}-aryl, or R_{18} and R_{19} together are -$(CH_2)_e$- wherein e is an

integer from 2 to 6; R_{20} and R_{21} are each independently of the other linear or branched C_1-C_8-alkyl that may be substituted by C_1-C_4-alkoxy, or C_6-C_{10}-aryl-C_1-C_8-alkyl or C_2-C_8-alkenyl; or R_{20} and R_{21} together are $-(CH_2)_{f1}-Z_3-(CH_2)_{f2}-$ wherein Z_3 is a direct bond, -O-, -S- or $-NR_{26}-$, and R_{26} is H or C_1-C_8-alkyl and f1 and f2 are each independently of the other an integer from 2 to 4; R_{23} and R_{24} are each independently of the other H, C_1-C_8-alkyl, C_3-C_8-cycloalkyl, benzyl or phenyl; and a, a1, b1, b2 and b3 are each independently of the other 0 or 1; subject to the provisos that b1 and b2 are each 0 when R_{15} is H; that the total of (b1+b2+b3) is not exceeding 2; and that a is 0 when R_{12} is a direct bond.

11. A composite material according to any one of claims 1 to 10, wherein according to (b) a hydrophilic macromonomer of the formula



(1),

is applied, wherein R_1 is hydrogen, C_1-C_6-alkyl or a radical -COOR';

R, R' and R_1' are each independently of the other hydrogen or C_1-C_6-alkyl;

A is a direct bond or is a radical of formula

$-C(O)-(A_1)_n-X-$ (2a) or

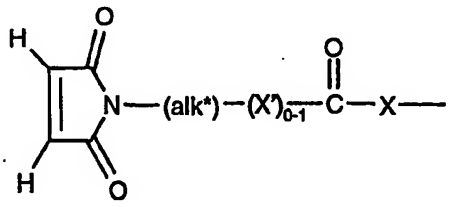
$-(A_2)_m-NH-C(O)-X-$ (2b); or

$-(A_2)_m-X-C(O)-$ (2c); or

-C(O)-NH-C(O)-X- (2d); or

$-C(O)-X_1-(alk^*)-X-C(O)-$ (2e); or

A and R_1, together with the adjacent double bond, are a radical of formula



(2f),

A_1 is $-O-C_2$-C_{12}-alkylene which is unsubstituted or substituted by hydroxy, or is $-O-C_2$-C_{12}-alkylene-NH-C(O)- or $-O-C_2$-C_{12}-alkylene-O-C(O)-NH-R_{11}-NH-C(O)-, wherein R_{11} is linear or branched C_1-C_{18}-alkylene or unsubstituted or C_1-C_4-alkyl- or C_1-C_4-alkoxy-substituted C_6-C_{10}-arylene, C_7-C_{18}-aralkylene, C_6-C_{10}-arylene-C_1-C_2-alkylene-C_6-C_{10}-arylene,

C_3-C_8-cycloalkylene, C_3-C_8-cycloalkylene-C_1-C_6-alkylene, C_3-C_8-cycloalkylene-C_1-C_2-alkylene-C_3-C_8-cycloalkylene or C_1-C_6-alkylene-C_3-C_8-cycloalkylene-C_1-C_6-alkylene ;

A_2 is C_1-C_8-alkylene; phenylene or benzylene;

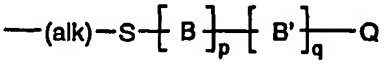
m and n are each independently of the other the number 0 or 1;

X, X_1 and X' are each independently of the other a bivalent group -O- or -NR", wherein R" is hydrogen or C_1-C_6-alkyl;

(alk*) is C_2-C_{12}-alkylene;

and (oligomer) denotes

(i) the radical of a telomer of formula



(3a),

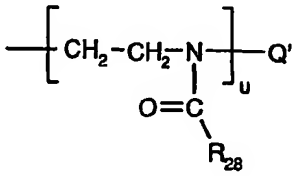
wherein (alk) is C_2-C_{12}-alkylene,

Q is a monovalent group that is suitable to act as a polymerization chain-reaction terminator,

p and q are each independently of another an integer from 0 to 250, wherein the total of (p+q) is an integer from 2 to 250,

and B and B' are each independently of the other a 1,2-ethylene radical derivable from a copolymerizable vinyl monomer by replacing the vinylic double bond by a single bond, at least one of the radicals B and B' being substituted by a hydrophilic substituent; or

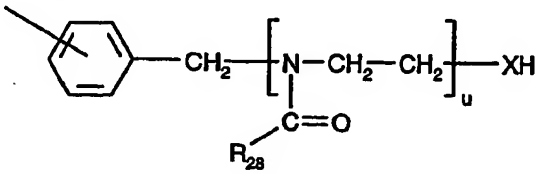
(ii) the radical of an oligomer of the formula



(3b),

wherein R_{28} is hydrogen or unsubstituted or hydroxy-substituted C_1-C_{12}-alkyl, u is an integer from 2 to 250 and Q' is a radical of a polymerization initiator; or

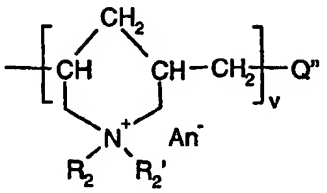
(iii) the radical of formula



(3b'),

wherein R_{28}, X and u are as defined above, or

(iv) the radical of an oligomer of formula



(3c),

wherein R_2 and R_2' are each independently C_1-C_4-alkyl, An^- is an anion, v is an integer from 2 to 250, and Q" is a monovalent group that is suitable to act as a polymerization chain-reaction terminator; or

(v) the radical of an oligopeptide of formula

$$-(CHR_4\text{-}C(O)\text{-}NH)_t\text{-}CHR_4\text{-}COOH \quad (3d) \text{ or}$$

$$-CHR_4\text{-}(NH\text{-}C(O)\text{-}CHR_4)_t\text{-}NH_2 \quad (3d'),$$

wherein R_4 is hydrogen or C_1-C_4-alkyl which is unsubstituted or substituted by hydroxy, carboxy, carbamoyl, amino, phenyl, o-, m- or p-hydroxyphenyl, imidazolyl, indolyl or a radical -NH-C(=NH)-NH_2 and t is an integer from 2 to 250, or the radical of an oligopeptide based on proline or hydroxyproline; or

(vi) the radical of a polyalkylene oxide of formula

$$-(alk''\text{-}O)_z\text{-}[CH_2\text{-}CH_2\text{-}O]_r\text{-}[CH_2\text{-}CH(CH_3)\text{-}O]_s\text{-}R_{30} \quad (3e),$$

wherein R_{30} is hydrogen or C_1-C_{24}-alkyl, (alk") is C_2-C_4-alkylene, z is 0 or 1, r and s are each independently an integer from 0 to 250 and the total of (r+s) is from 2 to 250; or

(vii) the radical of an oligosaccharide;

subject to the provisos that

A is not a direct bond if (oligomer) is a radical of formula (3a);

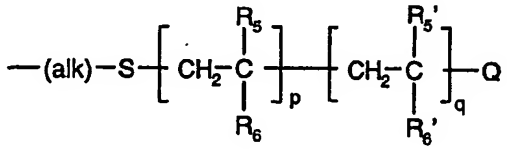
A is a direct bond if (oligomer) is a radical of formula (3b');

A is not a radical of formula (2c) or (2e) if (oligomer) is a radical of formula (3b), (3c), (3d), (3e) or is the radical of an oligosaccharide;and

A is a radical of formula (2c) or (2e) if (oligomer) is a radical of formula (3d').

12. A composite material according to claim 11, wherein the hydrophilic macromonomer is a compound of formula (1), wherein R is hydrogen or methyl, R_1 is hydrogen, methyl or carboxyl, R_1' is hydrogen, A is a radical of the formula (2a) or (2b), and (oligomer) is the radical of a telomer of formula (3a).

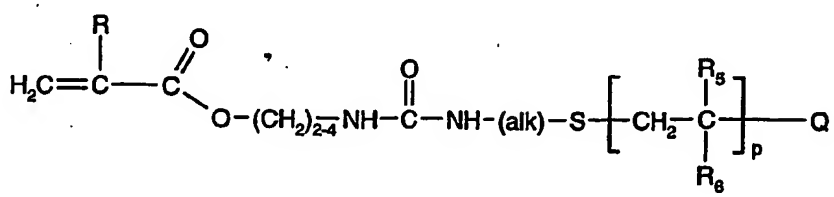
13. A composite material according to claim 11 or 12, wherein (oligomer) denotes a radical of formula (3a), and the radical -(alk)-S-$[B]_p$-$[B']_q$-Q is a radical of formula



(3a'),

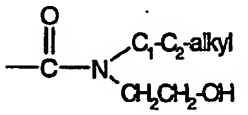
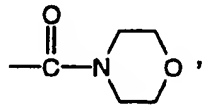
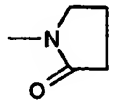
wherein (alk) is C_2-C_4-alkylene, R_5 and R_5' are each independently hydrogen or methyl, Q is a monovalent group that is suitable to act as a polymerization chain-reaction terminator, p and q are each independently an integer from 0 to 100 wherein the total of (p+q) is an integer from 5 to 100, and R_6 and R_6' are each independently a radical -COOY, wherein Y is C_1-C_2-alkyl, C_2-C_3-alkyl, which is substituted by hydroxy, amino or N,N-di-C_1-C_2-alkylamino, or is a radical -C_2-C_4-alkylene-NH-C(O)-O-G wherein -O-G is the radical of trehalose; a radical -CO-NY_1Y_2, wherein Y_1 and Y_2 are each independently of the other hydrogen or C_1-C_2-alkyl which is unsubstituted or substituted by hydroxy, or Y_1 and Y_2 together with the adjacent N-atom form a N-C_1-C_2-alkylpiperazino or morpholino ring; a heterocyclic radical selected from the group consisting of N-pyrrolidonyl, 2- or 4-pyridinyl, 2-methylpyridin-5-yl, 2-, 3- oder 4-hydroxypyridinyl, N-ε-caprolactamyl, N-imidazolyl, 2-methylimidazol-1-yl, N-morpholinyl and 4-N-methylpiperazin-1-yl; -COOH; -SO_3H; o-, m- or p-sulfophenyl; o-, m- or p-sulfomethylphenyl; a radical -$CONY_5Y_6$ wherein Y_5 is C_2-C_4-alkyl substituted by sulfo, and Y_6 is hydrogen; C_1-C_4-alkyl which is substituted by -$NR_9R_9'R_9''^+An^-$ wherein R_9, R_9' and R_9'' are each independently of another hydrogen or C_1-C_4-alkyl and An^- is an anion; a radical -$C(O)OY_7$ wherein Y_7 is C_2-C_4-alkyl, which is substituted by -$NR_9R_9'R_9''^+An^-$ and is further unsubstituted or substituted by hydroxy, wherein R_9, R_9', R_9" and $^+An^-$ are as defined; and a radical -C(O)O-CH_2-$CH(OY_8)$-CH_2-O-PO_2^--$(CH_2)_2$-$N(CH_3)_3^+$, wherein Y_8 is hydrogen or the acyl radical of a higher fatty acid.

14. A composite material according to any one of claims 11 to 13, wherein the hydrophilic macromonomer applied according to (b) is of the formula



(1b),

wherein R is hydrogen or methyl, (alk) is C_2-C_4-alkylene, R_5 is hydrogen or methyl, p is an integer of 5 to 50, Q is as defined, and R_6 is a radical $-CONH_2$, $-CON(CH_3)_2$,

$-CONH-(CH_2)_2-OH$,  ,  ,  ,

$-COO-(CH_2)_2-N(CH_3)_2$, or $-COO(CH_2)_{2-4}-NHC(O)-O-G$ wherein -O-G is the radical of trehalose.

15. A composite material according to any one of claims 1 to 14, wherein the polymerization of the monomers or macromonomers on the modified bulk material surface is initiated by the action of irradiation.

16. A composite material according to claim 15, wherein the polymerization is initiated by the action of UV radiation for a time period of 0.5 to 5 minutes.

17. A composite material according to any of claims 1 to 16, wherein the hydrophilic surface coating (b) is obtainable by grafting at least one macromonomer to the bulk material surface with formation of a bottle-brush-type structure composed of tethered chains.

18. A composite material according to any of claims 1 to 17, wherein the hydrophilic surface coating has a coating thickness of from 0.01 to 5 0 µm, and preferably from 0.1 to 1 µm.

19. A process for the manufacture of a composite material, which comprises the steps:
(a) providing an inorganic or organic bulk material having attached to its surface a polyionic material that comprises covalently bound initiator moieties for radical polymerization;
(b) applying a coating of one or more different ethylenically unsaturated hydrophilic monomers or macromonomers to the bulk material surface provided with the initiator radicals, and
(c) polymerizing the coating of unsaturated hydrophilic macromonomers thermally or by irradiation, preferably by UV radiation.

20. A process according to claim 19, wherein the polyionic material includes at least one bilayer, the bilayer comprising a first ionic polymer and a second ionic polymer having charges opposite of the charges of the first ionic polymer, said bilayer being applied to the bulk material surface by a dip method comprising the steps of (i) immersing the bulk material in a solution of the first ionic polymer; and then (ii) immersing the bulk material in a solution of the second ionic polymer having charges opposite to the charges of the first ionic polymer.

21. A process according to claim 20, wherein the first ionic polymer is an anionic polymer comprising carboxy groups or a salt thereof, and the second ionic polymer is a cationic polymer comprising primary or secondary amino groups or a salt thereof.

22. A process according to any one of claims 19 to 21, wherein the initiator moieties for radical polymerization are bound to the polyionic material by reaction of amino groups of the polyionic material with isocyanato groups of the initiator moiety.

23. A process according to any one of claims 19 to 22, wherein the inorganic or organic bulk material is a biomedical device, particularly a contact lens, intraocular lens or artificial cornea.

24. Biomedical device comprising a composite material according to any one of claims 1 to 18.

25. Biomedical device according to claim 24, wherein the biomedical device is a contact lens, intraocular lens or artificial cornea.

26. Use of a composite material according to any of claims 1 to 18 for the manufacture of an ophthalmic device, particularly for the manufacture of a contact lens, intraocular lens or artificial cornea.

INTERNATIONAL SEARCH REPORT

Int onal Application No
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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G02B1/04 A61L27/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G02B A61L C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, PAJ

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
8 October 2001	17/10/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Depijper, R

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